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Full Length Article

Size dependent photoluminescence property of hydrothermally synthesized crystalline carbon quantum dots

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ABSTRACT

In this work, simple hydrothermal synthesis of water soluble Carbon quantum dots (CQDs) of different sizes has been reported. The effect of synthesis temperature and synthesis time on the particle size has also been shown. The structures of all the as-prepared samples were studied by field emission scanning electron microscope and high resolution transmission electron microscope. Fourier transformed infrared spectrophotometer analyzes the different bonding present in the sample whereas Raman spectrophotometer quantifies the hybridization state of the prepared samples. UV–vis spectrophotometer gives the variation of absorbance of all the samples with wavelength. Dynamic light scattering study shows the variation of particle size with deposition condition and corresponding zeta potential gives the idea about the stability of the CQD solutions. The photoluminescence (PL) properties of the as prepared CQDs were also studied in detail. It is noticed that with the increase of excitation wavelength, the PL emissions for the different samples were red shifted. The results have been explained in terms of the excitation dependent emission, variations in size of the CQD and presence of different functional groups on the surface of CQDs.

1. Introduction

In the last few decades, carbon based nanomaterials have gained a lot of attention due to their unique electronic, mechanical, physical and optical properties. The different Carbon nanostructures include one dimensional carbon nanotubes (CNTs), nanofibers (CNF), two dimensional graphene, three dimensional diamond, fullerene or zero dimensional carbon dots (CDs). Of which CDs are basically defined as the spherical carbon particles having dimension between 1 and 10 nm. CDs have gained attention of the modern researchers due their unique electronic and optical properties.

CDs are mainly classified into graphene quantum dots (GQDs), carbon quantum dots (CQDs) and polymer dots (PDs). Of which CQDs are composed of both the sp^2 and sp^3 hybridized carbon. CQDs have many applications as a photocatalytic agent and in optoelectronic devices or in the field of bio-imagining [1–4]. Also there are a number of reports regarding the exciting photoluminescence (PL) property of CQDs, and it has been seen that the variation of CQD size is one of the key process to tune the PL properties of this material [5–7]. CQD is a material of interest for its other favorable properties like chemical inertness, low toxicity and high stability.

There are a number of reports present regarding the synthesis of CQDs from different organic compounds like sucrose, glucose, neem and glycol. CQDs can be synthesized by different top down or bottom up techniques [6,8,9]. For instance, Shcipunov.et.al prepared CQDs from Chitin by hydrothermal technique and Li.et al. reported the preparation of the same by pyrolytic synthesis technique [10,11]. CQDs can also be prepared from carbon nanotubes, graphene and from different natural resources like grass and leaves etc. However, most of the synthesis techniques often require use of toxic materials and multiple complex steps and they have low quantum yield (QY). Sahu.et.al reported the preparation of CQDs from orange juice with exciting bio imaging application and the formation involved hydrothermal carbonization [12].

It is possible to synthesize QDs from different semiconductor like Silicon also [13]. II–VI semiconductor quantum dots have shown fascinating PL properties but the synthesis techniques for preparing such QDs often require the use of toxic and hazardous materials.

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Thus CQDs have advantages over existing semiconductor QDs for their environment friendly, cost effective and high yield synthesis process [14]. From this point of view, CQDs can be a good substitute for semiconductor QDs. Although the optical characteristics of CQDs were investigated previously, there are not many reports regarding the size dependent PL properties of hydrothermally synthesized CQDs. This fact is rather surprising as CQDs have established themselves to be one of the most important electronic and photonic materials owing to quantum confinement, size dependent PL property and its wide band gap. The PL property of QDs is dependent on the size of the quantum dots and the sizes of the QDs are dependent on the synthesis time and synthesis temperature [6]. Thus the size dependent PL property of these CQDs would certainly be interesting to study.

Keeping all these in mind here we have reported the synthesis of the water soluble CQDs from sucrose by a simple low-temperature hydrothermal approach. This simple, high yield approach is capable of producing almost 60 mL solution containing CQDs evenly dispersed in single go. The CQDs prepared in this way are stable even after several months of preparation.

The PL response of the as prepared CQDs was studied by varying the excitation wavelengths. The excitation dependent PL properties have been shown and the corresponding CIE color spectrum (chromaticity diagram) were used to predict the CIE coordinates and approximate color of the emitted light from the CQD samples. Most importantly it is seen that the as prepared samples are so stable that the PL property remain unchanged even after several months of preparation.

2. Experimental and characterization

CQDs of different sizes have been prepared by a simple low-temperature hydrothermal process as described by Sahu. et al. [12]. In a typical experiment certain amount of water and ethanol was taken in a 100 mL Teflon lined autoclave reactor with stainless steel jacket. 1.5625 g sucrose was added to the solution and stirred for 30 min. The pH of the solution has been set to be 5.

The autoclave was then heated in an air oven for different temperature and time and subsequently the samples were left to cool normally. The solutions were centrifuged at 15,000 rpm for 45 min to prepare the water soluble CQDs. Course particles dissolved in the solution can be separated through filtration.

Sample S1 and S2 were prepared by heating the autoclave at 120 °C for 120 and 150 min. For the preparation of samples S3 and S4 the reaction time was 150 min and temperatures were 150° and 180 °C.

It is to be noted that though initial concentration of all the samples was same, the samples S1 and S2 were colorless but S3 was a little yellowish whereas S4 was dark brown in color as shown in Fig. 1.

The as prepared samples were characterized by field emission scanning electron microscope (FESEM, Hitachi, S-4800), high resolution transmission electron microscopy (HRTEM, JEOL-JEM 2100), dynamic light scattering (DLS) measuring system, Fourier transformed infrared spectrophotometer (FTIR-8400S), Raman spectrometer (Witec, λ_{ex}=532 nm) and UV–vis spectrophotometer (Shimadzu UV-3600). Also the steady state photoluminescence measurement was carried out by Shimadzu RF5301 spectrofluorometer. The time resolved photoluminescence measurements were performed by Edinburgh FLS980 spectrometer with the help of time-correlated single-photon counting (TCSPC) apparatus using a 280 nm picosecond pulsed LED and an MCP as detector. Time resolved spectroscopic characterization was examined for 360 nm emission at 280 nm excitation for the determination of the excited state life time of the prepared carbon dot samples. The emitted color of the CQD samples was approximately predicted with the help of CIE color co-ordinates (chromaticity diagrams).

3. Results and discussion

3.1. DLS Study

Fig. 2 shows the distribution of particle size measured by DLS study for sample S1, S2 and S3 with corresponding Zeta potential for all the samples tabulated in Table 1. It is seen that the average

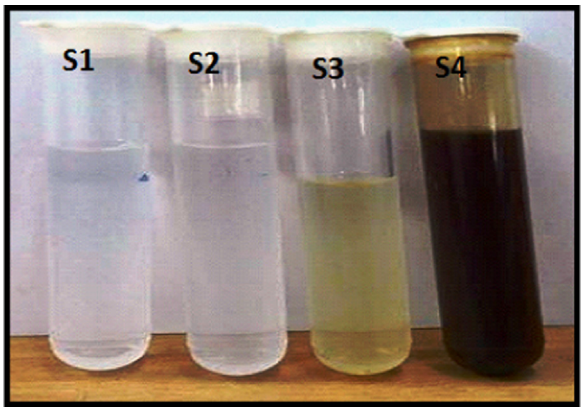

Fig. 1. Digital picture of all the four samples. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

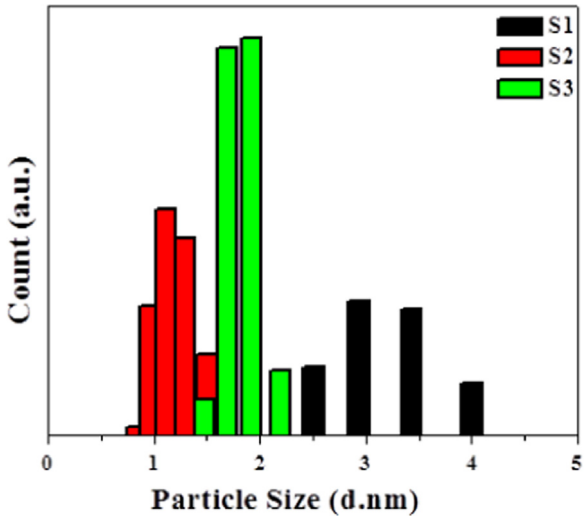

Fig. 2. Particle size distribution of sample S1, S2, S3 as measured by DLS analysis.

Table 1
Comparison of synthesis time, synthesis temperature, Zeta potential, approximate diameter calculated by DLS method and diameter measured in HRTEM images for the CQD samples S1, S2, S3 and S4.

Sample	Synthesis details		Zeta potential	Diameter from DLS	Diameter from HRTEM
	Synthesis time	Synthesis temp.			
S1	120 min	120°C	0.004865 mV	3-4 nm	3–6 nm
S2	150 min	120°C	0.456 mV	2-3 nm	1.9–3 nm
S3	150 min	150°C	−0.207 mV	4-5 nm	4–8 nm
S4	150 min	180°C	−0.0561	–	5-9 nm