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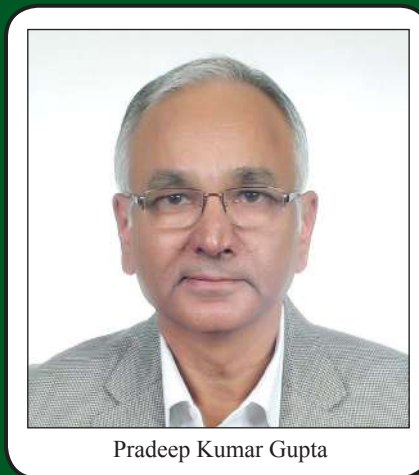
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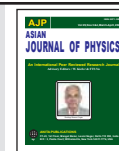


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Origin of photoluminescence in carbon “Dots”

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This article is dedicated to Prof Pradeep K Gupta for his contributions to optics and photonics
with biomedical applications

Using the method of dialysis a differentiation has been made between the photophysical properties of carbon dots and the photoluminescent impurities that are inherently associated with them owing to the various synthetic methodologies developed for the easy and inexpensive synthesis of these comparatively newer class of organic nanoparticles. © Anita Publications. All rights reserved.

Keywords: Dialysis, Photoluminescence, Photoluminescence lifetime, Carbon dots

1 Introduction

Ever since the discovery of Buckminsterfullerene was reported in the seminal paper by Kroto *et al* [1], nanocarbon has continued to fascinate and intrigue researchers from different fields [2,3]. Carbon dots (C-dots), the newest addition to the family of nanocarbons, have been discovered accidentally, more than a decade ago [3]. They are discrete, quasispherical nanoparticles with diameters less than 10 nm [4-7]. C-dots are photoluminescent and hold the promise to be potentially better substitutes of conventional fluorophores, as they do not get photobleached [8,9] and moreover, are biocompatible [9,11], and exhibit strong two photon excited luminescence [6,12]. They can be prepared by unbelievably simple techniques and this adds further to the interest in them [13-15]. Interestingly, the photoluminescence spectra of C-dots exhibit a marked dependence on excitation wavelength [16-18]. A number of mechanisms has been proposed to explain the photophysical properties of C-dots including contribution of surface defects [19,20] and bandgap emission emanating from conjugated pi-domains [21,22]. However, a consensus is yet to be reached on the mechanism of photoluminescence of C-dots. This is the motivation of the work presented in this paper, the aim of which is to perform a systematic study of the excited state dynamics involved in the luminescence of C-dots. The paper has been organized as follows: The first step consists of synthesis of cleaning a C-dot system by bottom-up approach using simple organic precursor (acetic acid in this work) and subsequent cleaning of the system by dialyzing it thoroughly. The next step consists of making a comparative examination of the photophysical properties of the purified system and the separated “impurities” for the assessment of contributing factors towards the observed photoluminescence. As we will see in the results and the discussion section, this approach helps us understand to a considerable extent, the origin of photoluminescence in the C-dots synthesized using this route.

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2 Experiments

2.1. Synthesis and characterization of C-dots

The C-dots used in this study are synthesized using the one step method reported by Wang and co-workers [15]. 1 ml of acetic acid (sigma-Aldrich, now Millipore Sigma) containing 100 μ l of water is added to 2g of phosphorus pentoxide (P_2O_5) (S D Fine-Chem Limited, Mumbai). Water induces hydroxylation of P_2O_5 which is a highly exothermic process. Heat released during this reaction initiates the carbonization of the acetic acid precursor leading to the generation of carbon nanoparticles typically of 4 – 6 nm size. The synthesized nanoparticles have been characterized using field emission transmission electron microscope (FEG-TEM, JEOL JEM-2100F). Raman measurements were performed on Horiba JobinYvon, (Model HR800-UV) confocal micro-Raman spectrometer. Steady state spectra have been recorded on JASCOV530 spectrophotometer and Varian Cary Eclipsefluorimeter. Time correlated single photon counting (TCSPC) measurements for determination of photoluminescence lifetime are carried out on a TCSPC system from IBH, UK. The decays have been collected in a magic angle configuration with respect to excitation beam and have been fitted to a sum of exponentials, $I_t = I_0 \sum A_i \exp(-t/\tau_i)$, where I_0 and I_t are the fluorescence intensities at time zero and t after excitation, respectively and A_i is the amplitude of the i^{th} decay. The decay traces were fitted using IBH DAS software (version 6.2) by iterative deconvolution method.

2.2. Dialysis of C-dots

The solid mass generated during the synthesis of C-dots by the process mentioned above is dissolved in water with mechanical stirring and is allowed to settle. The supernatant is decanted and further centrifuged to remove bigger particles that may still be present. Then, it is dialysed against deionized water 500 times its volume using a 3.5 kDa MWCO dialysis membrane (SnakeSkin™ Dialysis Tubing, ThermoFisher). The dialysis is performed for seven days, after which the sample is found to be lighter in color than the crude sample. The TEM images confirm the presence of Carbon dots in the solution recovered from the dialysis bag.

3 Results and Discussion

The bottom-up approach of synthesis of C-dots yield spheroidal particles as confirmed by the TEM images (Figs 2(a,b)). Raman measurements performed on the particles point towards existence of graphitic domains in the C-dots as evident from observation of signature D-band (1340 cm^{-1}) and G band (1584 cm^{-1}) (Fig 2(c)). The particle size analysis performed on the TEM images of the C-dots reveal that particles having diameter less than approximately 4 nm are also eluted from the dialysis bag (Figs 2(d,e,f)). However, the electronic spectra of the sample post dialysis is found to be significantly different from that of the crude sample as well as the elutant (Figs 2(g-i)). The spectral features of the crude and the elutant samples are almost identical.

The features in the absorption spectra present in the crude and the elutant sample almost disappear post dialysis and the spectrum is dominated by scattering. The emission maxima do not change, but there is a significant change in the spectral width and excitation wavelength-dependence of emission intensities. Prior to dialysis, the spectrum is narrower and the maximum peak intensity is achieved for excitation at 400 nm. After dialysis, however, broader spectra are obtained. Moreover, excitation at 250 nm results in maximum emission intensity in the sample after dialysis. The excitation spectra before and after dialysis are separated from each other by about 200 nm (Fig 1(i)). This implies that the predominant emissive species in the crude sample is removed to a large extent by dialysis. C-dots as a source of emission would be in contradiction to this observation. Another important point to note is that the excitation spectrum before dialysis is significantly different from the corresponding absorption spectrum, while after dialysis, it is in a much better agreement

with the absorption spectrum (Figs 1 (g-i)). This observation lends credence to the notion that process of dialysis gets rid of highly photoluminescent impurities to a good extent. This argument further gets support from a comparison of absorbance-corrected emission spectra pre- and post-dialysis, for excitation at 250 nm and 400 nm (Figs 2 (a, b)). For 400 nm excitation, the decrease in the intensity of emission is dramatic. Such changes in intensity can arise out of change in the number and/or nature of fluorescent species.

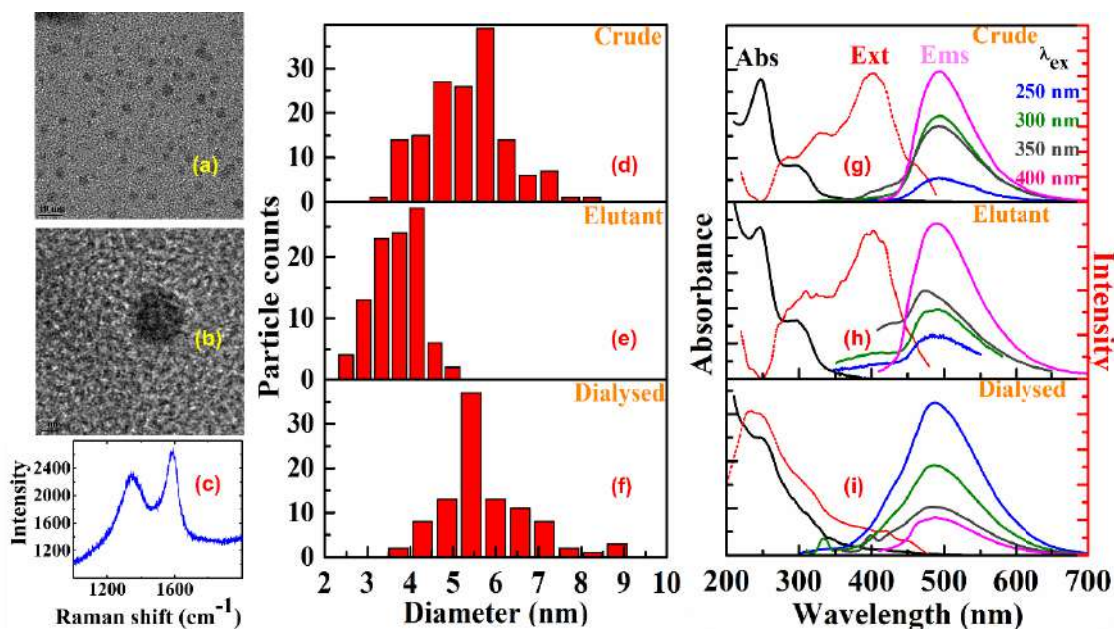


Fig 1. (a) TEM images of dialyzed C-dots (scale bar is set to 10 nm) (b) a single C-dot (scale bar set to 2nm) (c) Raman spectrum of synthesized C-dots (633 nm excitation, 1 second acquisition time with an average of 3 measurements) (d) particle size distribution of undialyzed C-dot sample (e) particle size distribution of C-dots present in the elutant recovered after the dialysis (f) particle size distribution of C-dots retained in the dialysis bag after dialysis was complete (g, h, i) Steady state photoluminescence properties of undialysed, elutant and dialysed sample. Absorption spectra has been shown in black and excitation spectra corresponding to 490 nm has been shown in red in all panels. Emission spectra are color coded for excitation corresponding to 250 nm (blue), 300 nm (olive), 350 nm (grey) and 400 nm (pink).

Table 1. Temporal parameters of crude and dialysed samples when excited at 265 nm and 375 nm, respectively. Emission was collected at 490 nm.

λ_{ex} (nm)	Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	χ^2
265	Crude	3.3	6.3	–	0.65	0.35	-	1.16
	Dialysed	1.6	5.2	–	0.70	0.30	-	1.06
375	Crude	1.2	6.7	–	0.48	0.52	-	1.13
	Dialysed	0.4	1.5	5.1	0.40	0.40	0.20	1.01

Time resolved measurements of the photoluminescence also reveal marked differences between the Time resolved measurements of the photoluminescence also reveal marked differences between the dependent for the crude sample. Also, the long components of the decays are almost the same for 265 nm

and 375 nm excitation. An additional short component is observed for 375 nm excitation, possibly due to scattering (Fig 2(c,d), Table 1)).

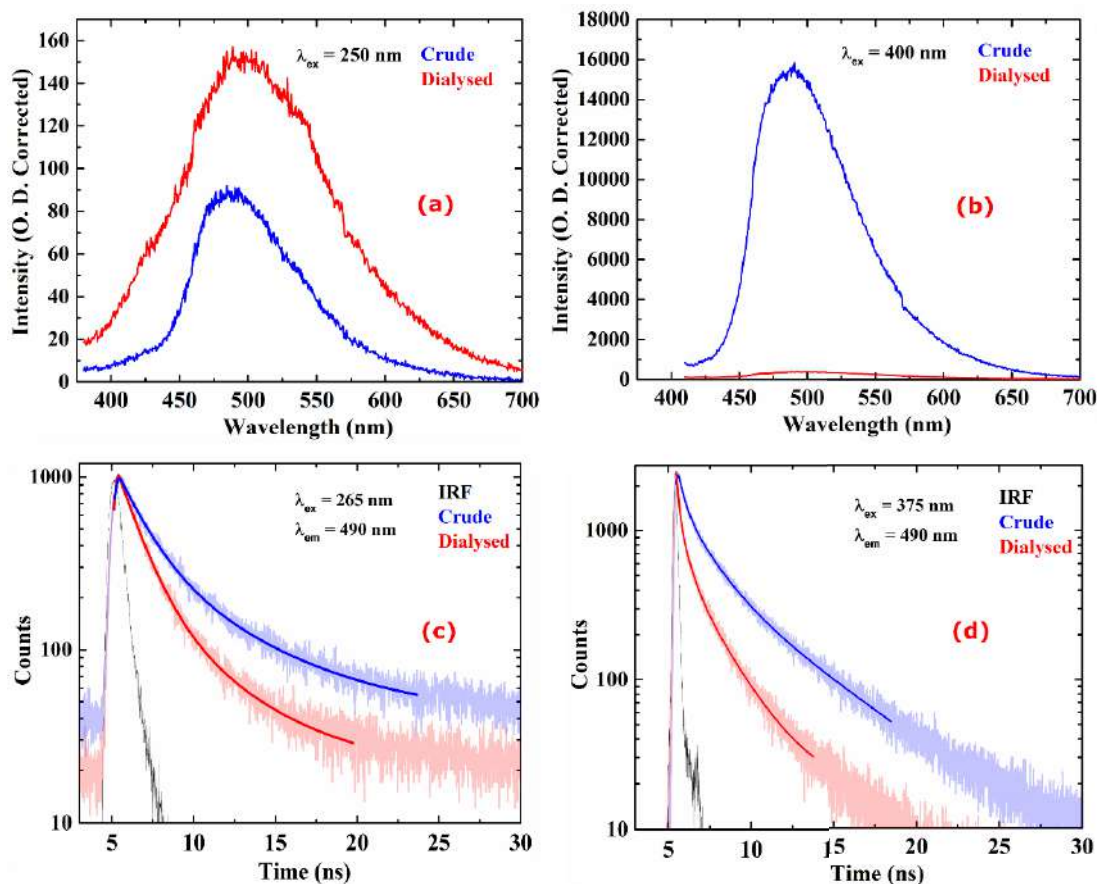


Fig 2. (a) O.D. corrected emission spectra of crude and dialysed sample excited at 250 nm (b), O.D. corrected emission spectra of crude and dialysed sample 400 nm (c) photoluminescence decay traces collected at 490 nm ($\lambda_{ex} = 265$ nm) (d) photoluminescence decay traces collected at 490 nm ($\lambda_{ex} = 375$ nm). All steady state spectra and decay traces are color coded for crude (blue) and dialysed (red) samples.

4 Conclusion

It appears that the source of bulk of the photoluminescence emanating from the Carbon dots synthesized using acetic acid as the precursor is molecular in nature rather than a quantum confinement phenomenon (as in case of traditional inorganic quantum dots) or a surface phenomenon. The synthesized Carbon dot system gets cleaned up to a large extent by dialysis, which indicates that either the major emission is really due to strong fluorophores that adhere to the surface of carbon dots, or due to much smaller nanoparticles that are lost in the process of dialysis.

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