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Observation of fluorescence from non-functionalized carbon nanoparticles and its solvent dependent spectroscopy

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ABSTRACT

We report solvent dependent spectroscopic study of unique non-functionalized fluorescent carbon nanoparticles (NCNPs) dispersed in 15 organic solvents: aromatic (three), hydrogen bonded (five) and aprotic (seven). Absorption spectra were found to be independent of the solvent nature, with absorption bands located around 430, 405 and 385 nm whereas photoluminescence (PL) spectra exhibited considerable solvent dependence with PL emission peaks lying in the region 405 to 500 nm. Emission life time measured by time resolved fluorescence spectroscopy revealed that in aromatic solvents the average lifetime (τ_{av}), did not change significantly with solvent polarity, which was, typically 4–5 ns under the excitation of 405 nm. In hydrogen bonded solvents, τ_{av} was observed to decrease with solvent polarity, but in case of aprotic solvents, τ_{av} was observed to increase with solvent polarity for a particular excitation. Emission data in hand revealed possible quantum confinement of these nanoparticles inside the cavity of rings of THF, p-xylene, benzene and toluene molecules.

1. Introduction

Fluorescent carbon nanoparticles have found promising applications in nanotechnology, bio-imaging, bio labeling, and drug delivery [1–4]. Fluorescent CNPs are poorly studied due to lack of reliable preparative methods. Common route for making fluorescent carbon nanoparticles includes laser ablation of graphite [5], creation of point defects in diamond [6] and wet electrochemical methods [7]. Recently, soot originated carbon nanoparticles (CNPs), has been rediscovered as a new class of carbonaceous nanostructures with interesting properties [8,9]. It is very easy and inexpensive to produce carbon soot that is rich in nanostructures. However, in order to improve their aqueous dispersibility and fluorescence yield, these particles are often treated with oxidative acid protocol. The synthesis and luminescence study of various allotropes of carbon nanostructures, which includes soot derived particles, is discussed in excellent details in a review by Baker et al. [10]. For example, Liu et al. [9], and Wang et al. [11], collected soot by placing a piece of aluminum foil or a glass plate atop a burning candle. The collected soot was followed by an oxidative acid treatment to introduce OH and CO_2H groups to the surfaces to make them negatively charged and hydrophilic. Recently Esteves da Silva et al. [12] also reported carbon dots (CDs) comprises with strongly fluorescent, emission-color-tuning and non-blinking nanoparticles with great analytical and bioanalytical potential. In all techniques used so far, the CNPs were surface modified in order to achieve fluorescence. In contrast, we adopted a single step preparation protocol that did not require surface modification. On the other hand, the understanding of fluorescence emanating from carbon nanoparticles can be considered incomplete. In general, the organic surface passivation details are not sufficient to aid understanding of the surface states beneficial for fluorescence emission. The origin of fluorescence in organic solvents is due to the trapping of excitation energy on the nano-structure surface, is reported [5,9,13,14].

The fluorescent single-walled carbon nanotubes (SWCNT) are known for a long time. These samples are normally prepared through rigorous protocols that make the product expensive. The contribution of the surrounding environment on the spectroscopic properties of these is not well understood [14–19]. In several studies SWCNTs were suspended in organic solvents to study their characteristic PL emission [14,19] features, but no such study has ever been carried out on carbon nanoparticles prepared from soot. Dispersing CNPs prepared from soot in organic as well in aqueous solvents remains a challenging task. Therefore, the search for benign fluorescent carbon nanoparticles through an easy and inexpensive route and probing the effect of dispersion media has become an urgent challenge. The objective of the present work was to investigate the solvent effect on the fluorescence properties of these nanoparticles. This is the first report where a systematic study of non-functionalized fluorescent

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carbon nanoparticles made from lamp soot and dispersed in a wide range of organic solvents is presented. The potential usefulness of carbon nanoparticles as a luminescent material sensitively depends on their emission lifetime. In order to establish the influence of solvent structure and polarity on fluorescent behavior, time resolved fluorescence spectroscopy, which provides very interesting information on the emission lifetime, shape, size and rotational properties of nanoparticles in solution was carried out.

2. Experimental details

The carbon nanoparticles were prepared from lamp soot, which is broadly described in our previous work [20,21] and the exact protocol is provided elsewhere [22]. Typically, 0.1% (w/v) of carbon powder material was dispersed in 15 different organic solvents to get the required stock dispersions. These dispersions were stirred with a magnetic stirrer for 6 h to make these homogeneous. The dispersions were allowed to stand for overnight to enable the larger particles and clusters to sediment, and settle at the bottom. This generated optically clear and stable dispersions and was stored in an air tight ultra-clean borosilicate glass bottles for future use. We have used three different classes of solvents in these studies: aromatic, hydrogen bonded and aprotic. In aprotic family, solvents chosen were: diethyl ether, ethyl acetate, tetrahydrofuran (THF), acetone, dimethyl sulfoxide (DMSO), dimethyl formide (DMF), and acetonitrile. In hydrogen bonded category, we used acetic acid, methanol, ethanol, propanol, and butanol, and in the aromatic class benzene, p-xylene and toluene were chosen. This covered the entire spectrum of common organic solvents used in pharmaceutical and biological applications. All solvents examined in this study were spectroscopic grade (purity 99.9%) obtained from Merck and were degassed before using. All the sample preparations and measurements were carried out at room temperature (25 °C, and RH < 50%).

Steady-state absorption and PL emission spectra were recorded using a Cecil CE-7200 (Cecil Instruments, UK) UV–vis spectrophotometer and Varian Cary Eclipse fluorescence spectrometer respectively. For steady-state PL studies, the samples were excited at 375, 381, 405 and 429 nm wavelengths. Time resolved fluorescence spectroscopy (TRFS) is a more sensitive technique than the steady-state absorption or fluorescence spectroscopy, and is a very good method to probe solvent environment effect on the kinetics or dynamics of nanoparticles and macromolecules in solution. Further details about TRFS and its data analysis can be found elsewhere [23]. The lifetime decay and anisotropy experiments were performed using time-correlated single photon counting (TCSPC) setup (FL920, Edinburgh Instrument). All samples were excited with diode lasers and the decays were collected at emission peak wavelength at magic angle polarization (55°). Here, we have used picosecond TRFS to probe the solvent effect on the lifetime of relaxations. All the measurements have been done with 100 nm TAC (Time to Amplitude Convertor) at excitation wavelengths of 375 and 405 nm. The time resolution for TCSPC setup was ~120 ps (measured with LUDOX solution). All the emission decays were collected at emission peak wavelengths, and the data were fitted best to the triple-exponential fitting function (goodness-of-fit ($\chi 2$) values are given in Tables 1 and 2) given by

$$F(t) = a_0 + a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3) \quad (1)$$

where a_0 is the time shift between IRF (Instrument Response Function) and sample. The relaxation times are τ_1, τ_2, and τ_3, and these correspond to various lifetimes of characteristic excited states. $F(t)$ could not be fitted either to a single or double exponential function. The average time constant or correlation time is given as

$$\langle \tau \rangle = \sum_i a_i \tau_i \quad (2)$$

Time resolved fluorescence polarization anisotropy is a very powerful tool, which provides information on the size and shape of fluorescing particles, and characteristics of surrounding environment. The technique is based on the fact that linearly polarized light preferentially excites those molecules or particles whose transition dipole moment is parallel to the light field. Subsequently, due to rotational diffusion of the excited particles, their average dipole moment acquires a non-vanishing component perpendicular to the exciting field and the same occurs to the polarization direction of fluorescence light. By measuring the characteristic time for such a depolarization process, it is possible to determine the size of fluorescent particles.

The time-dependent fluorescence anisotropy is characterized by a ratio, $r(t)$ and for a linearly polarized exciting field it is defined as.

$$r(t) = \frac{I_{||}(t) - G I_{\perp}(t)}{I_{||}(t) + 2G I_{\perp}(t)} \quad (3)$$

where $I_{||}(t)$ and $I_{\perp}(t)$ are the polarized components of the time resolved fluorescence intensity, respectively, parallel and perpendicular to the excitation field. The factor, G is the correction factor that accounts for the different efficiencies of the optical components for the two polarizations, and it can be easily determined.

Table 1
Emission lifetime, steady-state PL emission peak and hydrodynamic radius of NCNPs in different solvents at excitation wavelengths of 375 nm. The data are listed out in according to solvent class and $F(\varepsilon_0,n)$ value.

Solvent Class	Solvents	$F(\varepsilon_0,n)$	a_1 (%)	τ_1/ns	a_2 (%)	τ_2/ns	a_3 (%)	τ_3/ns	τ_{av}/ns	R_h/ nm	Emi. Wav./nm
Aromatic	Benzene	0.01	27.5	1.83	51.1	5.93	21.4	15.73	6.9	1.90	475
	p-Xylene	0.01	30.8	1.82	53.4	6.32	15.7	16.83	6.6	1.84	473
	Toluene	0.02	25.9	1.48	57.9	6.95	16.1	16.92	7.1	1.74	500
Hydrogen Bonded	Acetic Acid	0.40	21.1	1.20	52.9	6.12	25.9	17.72	8.1	1.54	430
	Butanol	0.61	29.0	1.25	50.3	6.06	20.6	17.63	7.0	0.93	472
	Propanol	0.63	27.8	1.40	48.2	6.12	23.9	18.01	7.6	1.16	432
	Ethanol	0.67	22.5	1.45	55.7	6.16	21.8	15.82	7.2	1.68	430
	Methanol	0.71	44.8	1.00	39.3	6.30	15.9	15.92	5.5	1.86	432
Aprotic	Diethyl ether	0.30	60.0	0.93	29.9	5.50	9.9	16.04	3.8	2.90	430
	Ethyl Acetate	0.40	59.2	0.91	31.5	5.37	9.34	13.65	3.5	2.03	431
	THF	0.44	37.1	0.99	45.3	6.00	17.6	15.62	5.8	1.97	495
	Acetone	0.65	28.2	1.07	54.2	5.62	17.6	14.28	5.8	2.44	485
	DMSO	0.66	24.9	0.94	43.6	5.65	31.5	21.97	9.6	1.10	432
	DMF	0.67	34.8	1.04	44.5	5.65	20.6	19.12	6.8	1.76	432
	Acetonitrile	0.71	23.0	1.31	61.7	5.65	15.2	14.95	5.9	2.47	438