International Journal of Thermal Sciences 126 (2018) 137–142

Contents lists available at ScienceDirect

International Journal of Thermal Sciences

journal homepage: www.elsevier.com/locate/ijts

Concentration dependent variation of thermal diffusivity in highly fluorescent carbon dots using dual beam thermal lens technique

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ARTICLE INFO

Keywords:
Fluorescent carbon dots
Ethylenediamine
Thermal diffusivity
Thermal lens technique

ABSTRACT

Thermal and optical properties of fluorescent carbon dots (CDs) prepared from citric acid anhydrous as the precursor and ethylenediamine as the passivation agent by microwave assisted synthesis technique is explored in the present study. Optical absorption and emission spectra of carbon dots reveal the presence of surface states with an absorption peak around 350 nm and emission around 450 nm. Fourier Transform Infra-Red (FT-IR) spectra also indicate the presence of surface states. Transmission electron microscopy images of these nano particles indicate an average particle size of 5.8 nm. Dual Beam thermal lens (TL) spectrometry, a highly sensitive photothermal technique, is employed to measure the thermal diffusivity of the carbon dots. Thermal diffusivity is found to decrease from 0.135 m^2/sec to 0.0365 m^2/sec as the weight percentage of carbon dots are increased from 0.0005 g/15 ml to 0.005/15 ml which can be attributed to the enhanced scattering of thermal waves with particle density in the medium. Studies reveal carbon dots to be promising candidates as thermal insulating materials.

1. Introduction

Carbon nano materials with size less than 10 nm, generally termed as carbon dots (CDs), due to their easy availability, cost effectiveness and harmless disposition are finding potential applications in optronics, catalysis, sensor and Bio-imaging [1–5]. CDs are advantageous as they possess high water solubility, robust chemical inertness, easy functionalization, high resistance to photobleaching, low toxicity and good bio-compatibility over traditional semiconductor quantum dots and organics dyes [6–8]. Recently optical properties of CDs are gaining much attention in the field of photonics due to their high fluorescence efficiency [9]. General preparations of carbon dots include top down and bottom up method [10–15]. In the present study CDs were prepared by microwave assisted synthesis technique.

Thermal diffusivity is an important thermo-optical property of the materials for applications as coolant or thermal insulator. Thermal properties of materials at nano scale may differ from that of bulk state. Several methods have been developed to measure thermal diffusivity of materials including laser flash technique, hot-wire technique, photoacoustic method, thermal–wave cavity technique and temperature oscillation technique [16–18]. The thermal lens technique is a sensitive method to measure the absolute value of thermal diffusivity in liquid samples [19]. This technique is advantageous for its ultra-sensitivity and other unique characteristics including small volume sample capability and dependence on thermo-optical properties of the solvent [20]. The unique characteristics of lasers, namely low-beam divergence, pure polarization, high spectral and spatial resolution, and its ability to be focussed to a diffraction-limited spot, have been fully exploited in thermal lens detection technique for microfluidic devices [21]. In this paper we report, the variation of thermal diffusivity of Carbon dots with varying particle density in an aqueous medium. To the best of our knowledge, there are no reports on thermal diffusivity studies of carbon dots except for some limited studies on thermal conductivity of carbon dots [22].

2. Theory

Dual beam thermal lens (TL) is a photo thermal technique highly sensitive to detect very small (as small as $10^{-8)}$ refractive index changes across the beam width resulting from a temperature variation of $\sim 10^{-5}$ °C in liquid [23]. A laser beam can thermally induce refractive index changes, which is the fundamental principle behind TL spectrometry [24]. The first measurement of the thermal lens effect was performed by Gordon et al., in 1965 using a single-beam apparatus [25].

The time dependent probe intensity in steady state is given by Ref. [26].

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https://doi.org/10.1016/j.ijthermalsci.2017.12.034
Received 22 May 2017; Received in revised form 29 December 2017; Accepted 29 December 2017

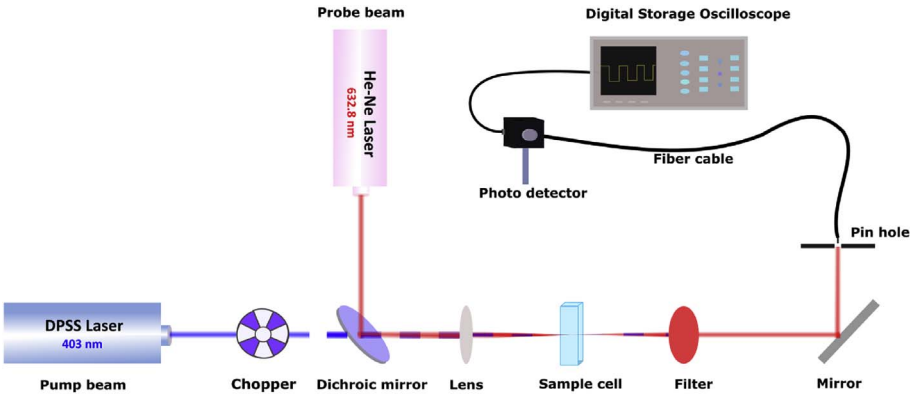

Fig. 1. Thermal Lens setup.

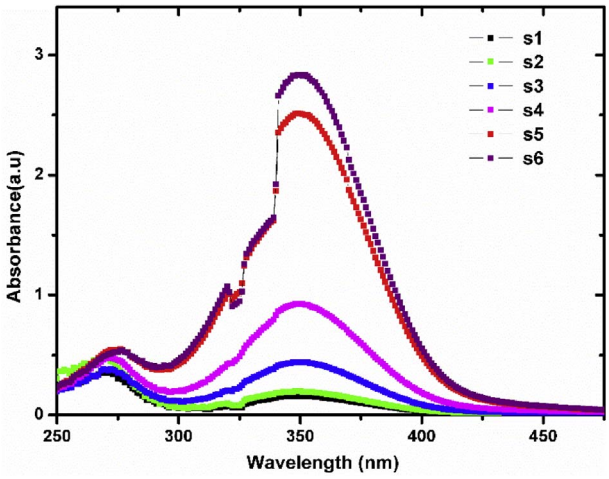

Fig. 2. Absorption spectra of CDs.

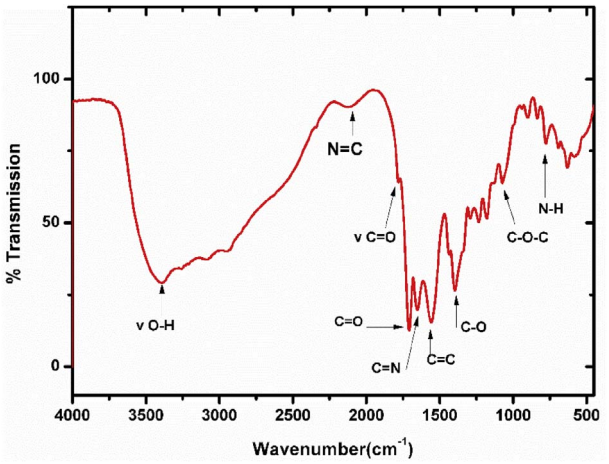

Fig. 3. FTIR spectrum of CDs.

$$I(t) = I_0\left[1 - \theta\left(1 + \frac{t_c}{2t}\right)^{-1} + \frac{1}{2}\theta^2\left(1 + \frac{t_c}{2t}\right)^{-2}\right]^{-1} \quad (1)$$

Here, the parameter θ is related to the thermal power radiated as heat (P_{th}) and other thermo-optic parameters of the material as

$$\theta = P_{th}\left(\frac{dn}{dt}\right)\lambda_L K \quad (2)$$

Where $\frac{dn}{dt}$ is the temperature dependence of the refractive index, λ_L is the laser wavelength and K is the thermal conductivity. θ can be calculated manually from the thermal lens signal through the expression $\theta = 1\text{-}\sqrt{1 + 2I}$, where $I = \frac{I_0 - I_\infty}{I_0}$, I_0 is the initial intensity of the probe beam and I_∞ is the intensity after the steady state. The parameter t_c, the characteristic time constant (t_c) for thermal lens formation is obtained by fitting equation (1) to the experimental data using calculated value of θ. The characteristic time constant leads to diffusivity D through the equation [21].

$$t_c = \frac{w^2}{4D} \quad (3)$$

Where w is the beam radius at sample position.

3. Experimental

3.1. Chemicals and materials

Citric acid anhydrous and ethylenediamine purchased from Sigma-Aldrich were used without further purification for the preparation of carbon dots. All the samples were prepared using ultra-pure water.

3.2. Preparation of ethylenediamine passivated carbon dots

For synthesizing carbon dots by microwave assisted synthesis technique, 1 g of citric acid anhydrous were dissolved into 1 ml of ethylenediamine (EDA) under stirring and heated using a domestic microwave oven with a power of 800 W for 4 min. The resulting brown precipitate formed were washed with acetone and dried. 0.0005 g (g) of the precipitate powder (carbon dots) were dispersed in 15 ml of water (Sample1) which were used for further investigations. Other samples prepared were s2 = 0.001 g/15 ml, s3 = 0.002 g/15 ml, s4 = 0.003 g/15 ml, s5 = 0.004 g/15 ml and s6 = 0.005 g/15 ml.

3.3. Characterization

Optical absorption spectra of the prepared Carbon dots were recorded using UV–Visible Spectrophotometer (Jasco V-570 UV/VIS/IR) and Fluorescence spectra using Cary Eclipse fluorescence spectrophotometer (Varian). Functional group present in the samples were analysed using Fourier Transform Infra-Red Spectrometer (FT-IR) (Thermo Nicolet model Avatar 370). High Resolution Transmission Electron Microscope (HR-TEM) images of carbon dots were recorded using JEOL (model JEM 2100). Elemental analysis were carried out using Elementar Vario EL III. X-ray photoelectron spectroscopic (XPS) analysis were carried out using KRATOS Axis Ultra (Kratos Analytical, UK).

3.4. Experimental setup

Thermal diffusivity measurements using dual beam thermal lens technique (Fig. 1) employs a 403 nm diode-pumped solid state (DPSS) laser with a power of 100 mW as the heating source and an intensity