



Research paper

Rheology of a carbon dot gel



Yiwen Ji^a, Yiqun Zhou^a, Eric Waidely^a, Alexandra Desserre^a, M. Hensley Marksberry^b, Charles C. Chusuei^b, Aijaz Ahmad Dar^c, Oyais Ahmad Chat^d, Shanghao Li^a, Roger M. Leblanc^{a,*}

^a Department of Chemistry, University of Miami, 1301 Memorial Drive, Cox Science Center, Coral Gables, FL 33146, USA

^b Department of Chemistry, Middle Tennessee State University, 440 Friendship Street, Murfreesboro, TN 37132, USA

^c Physical Chemistry Division, Department of Chemistry, University of Kashmir, Srinagar 190006, J&K, India

^d Department of Chemistry, University of Kashmir, Srinagar 190006, J&K, India

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ABSTRACT

Carbon dots have received great attention as a result of the favorable optical properties these nanoparticles possess. While much work has been done toward enhancing the optical properties, little investigation has been done on the materialistic properties of these nontoxic nanoparticles. Herein, a simple one-pot procedure for producing a highly viscous, thixotropic carbon dot gel material is presented. The carbon dots possess tunable emissions that are excitation-wavelength dependent and are an ideally viscous material.

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1. Introduction

The development of new carbon based nanomaterials has gained the interest of many research groups. The primary materials being developed include, but are not limited to, fullerene [1,2], carbon nanotubes [3], nanodiamonds [4] and carbon dots [5]. The latter, carbon dots, have been receiving an increasing amount of attention due to the favorable properties these particles possess. Carbon dots offer notable advantages over many similar nanoparticles, such as water solubility [6,7], tunable emissions [8], ease in synthetic approaches, and low toxicity [9].

The facile and extensive basis in which these nanoparticles are formed has been well investigated [10]. In 2006, Sun et al. [11] reported the first synthesis and characterization of carbon dots through acid oxidation of laser ablated graphite powder and cement, followed by passivation with polyethylene glycol. Synthesis techniques now consist of hydrothermal/solvothermal approaches [12–14], microwave synthesis [15–17], and electrochemical oxidation. Another appealing quality of carbon dot synthesis is the wide spectrum of starting materials that can be implemented, including inexpensive organic compounds/solvents [18], food products [19–21] and waste [22].

While a wide range of techniques have been applied to produce carbon dots, the nature of the generated products varies greatly. For example, Zhu et al. [23] report an increase in quantum yield (QY) from 20.9 to 80.6%, simply by changing the ratio of the starting materials. Many strategies have been developed to increase the

luminescence of these particles, with the most effective approach to date being doping with nitrogen [24]. Carbon dots are typically used in solution form, however, some groups further modify the carbon dots by embedding or conjugating them to other particles to enhance functionality [25,26]. With most carbon dot research of late being focused on increasing the optical capabilities, little work has been done on the material properties.

Herein, a facile one-pot synthesis of a carbon dot gel material is reported. The carbon dot gel is formed without the use of gelating agents. Addition of citric acid to boiling ethylenediamine yields a viscous, gel-like carbon dot product, with physical and chemical properties dependent upon the reaction conditions. The temperature and the duration of the reaction were shown to effect both the optical and materialistic properties.

2. Experimental

2.1. Materials

Citric acid (anhydrous, ≥99.5%) and ethylenediamine (99%) were purchased from Sigma Aldrich (St. Louis, MO) and were used without further purification. Quinine sulfate (99%) was obtained from Alfa Aesar (Ward Hill, MA). Dialysis was run through a Cellulose Ester membrane with molecular weight cut-off of 500–1000 Daltons purchased from Spectrum Laboratories Inc. (Rancho Dominguez, CA). Purified water was obtained from an Elga PURE-LAB Ultra water purifier (Woodridge, IL) with a resistivity of 18 MΩ·cm, surface tension of 72.6 mN m⁻¹, and pH 5.6 at 20.0 ± 0.5 °C.

* Corresponding author.

E-mail address: rml@miami.edu (R.M. Leblanc).

3. Methods

3.1. Preparation of carbon dots

For the preparation of carbon dot gels, three different temperatures and two different reaction times were chosen. The temperatures utilized were 120, 150, and 180 °C with reaction times being either 10 min or 5 h. The procedure for producing a carbon dot gel involves first heating ethylenediamine to near boil in a round bottom flask. Once boiling starts to occur, citric acid is added directly at a 1:14 molar ratio (citric acid:ethylenediamine) (Scheme S1). A jacketed condenser is added and the reaction is heated to the desired reaction temperature and refluxed for either 10 min or 5 h. Upon completion, excess ethylenediamine is evaporated off, leaving behind a thick, viscous yellow gel. The produced gel is then dissolved in DI water and placed into dialysis (MWCO 500–1000 Daltons) in water for 2 days, changing the water every 4–10 h. Upon completion of dialysis, the carbon dots can be used dissolved in water or isolated through evaporating off the water. The syntheses were triplicated to ensure the reproducibility.

3.2. Carbon dot characterization

Ultraviolet–visible spectroscopy measurements were obtained on an Agilent Cary 100 spectrophotometer (Santa Clara, CA, USA). Fluorescence measurements were carried out on a Horiba Jobin Yvon Fluorolog-3 (Kyoto, Japan) with slit widths set to 5 nm for both excitation and emission. The quantum yield was calculated via the luminescence measurement, using quinine sulfate as a reference standard, with the following equation: $\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$, where Φ is the quantum yield, I is the measured integrated emission intensity, η is the refractive index of the solvent, A is the optical density, and the subscript R refers to the reference standard. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer PHI 560 ESCA instrument using a non-monochromatic Mg K α anode, with a photon energy of 1253.6 eV, operated at 12 kV and 200 W. The carbon dot gel was prepared for XPS analysis via pipetting the gel onto a Ta foil sample holder and outgassing in a vacuum desiccator at 1 Torr at 120 °C until the solvent evaporated. The sample was then mounted onto the PHI 560 antechamber that was evacuated by using a Balzers 300 L/s turbomolecular pump at room temperature (21 \pm 1 °C) and then inserted into the

chamber. Complete coverage of the sample holder was assured by the absence of Ta 4f peaks in the survey spectrum (Fig. S1). High resolution XPS scans were obtained for the C 1s, O 1s and N 1s core levels. Calibration was performed using Au 4f_{7/2} and Cu 2p_{3/2} core levels for Au and Cu reference foils at 84.0 and 932.7 eV, respectively. The system pressure did not exceed 2×10^{-8} Torr during XPS scans. Atomic force microscopy (AFM) measurements were obtained on an Agilent 5420 AFM. Carbon dot samples were prepared for AFM analysis by first dissolving the gel in water to dilute the sample and to help mitigate the difficulty in transporting the gel. A single drop of the dilute carbon dots was placed onto a Mica slide and the water is allowed to evaporate (\sim 2 h). Once the slide is dry, the measurements were carried out using the tapping mode. Extracted profiles were reproduced several times to ensure the results reflected the sample as a whole.

3.3. Rheology measurements

The rheological properties of the carbon dot material were investigated by Anton Paar MCR-102 Rheometer equipped with a Peltier system of temperature control with an accuracy of ± 0.01 °C. The rheological measurements were performed using CP25-2 (diameter = 25 cm, cone angle = 1.998°) measuring system. Test modes employed were: the shear rate sweep, structure decomposition and regeneration (thixotropy) test and frequency sweep. In steady shear experiments, shear rate was varied from 0.1 to 10,000 s⁻¹. In controlled shear rate (CSR) profile for obtaining the thixotropic behavior, time dependent viscosities in three shear intervals viz low, high and again low shear in steps were plotted as a function of time. Stress sweep was performed on the carbon dot material at a constant frequency of 10 rad s⁻¹ to determine the linear viscoelastic region (LVR). The material was also subjected to a frequency sweep in LVR (stress of 0.1 Pa) to study the viscoelastic performance over a wide range of angular frequencies ranging from 0.01 to 600 rad s⁻¹. All the experiments were performed in triplicate to ensure reproducibility.

4. Results and discussion

The properties of the carbon dot gel produced were found to be dependent upon the reaction conditions applied. The UV–visible absorption spectra of the carbon dots dissolved in water (Fig. 1) shows broad absorptions in the range of \sim 250–400 nm, with two

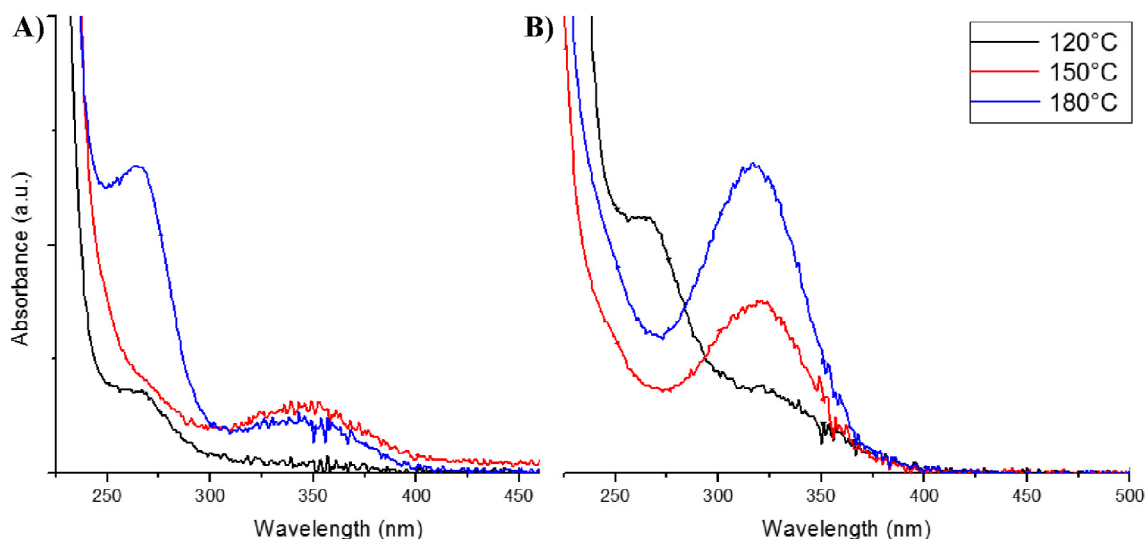


Fig. 1. Absorption spectrum for carbon dots prepared at different temperatures reacted for A) 10 min and B) 5 h.

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