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# Domestic pressure cooker as inexpensive hydrothermal vessel: Demonstrated utility for eco-friendly synthesis of non-toxic carbon dots☆

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ABSTRACT

We report on a simple and eco-friendly approach that employs a domestic pressure cooker as an inexpensive hydrothermal reactor for the batch synthesis of water-soluble, photoluminescent nanoscale carbon dots derived from benign and cheap commercial starting materials. The resulting carbon nanodots, which consist primarily of hydrophile-decorated amorphous carbon and boast bright, stable, excitation wavelength-dependent fluorescence, were shown to be viable cellular imaging agents for mice embryonic fibroblast cells, displaying little or no cytotoxicity for carbon dot concentrations up to 0.667 mg/mL. In addition, the carbon dots proved useful as nanoprobes for the fluorescence-based detection of environmentally-relevant heavy metal ions such as $Cu^{2+}$, displaying detection limits below 6 μM, sufficient to determine potable water safety (20 μM is the limit for safe drinking water set by the U.S. Environmental Protection Agency). More generally, these results highlight the utility of a household pressure cooker as a cost-effective hydrothermal vessel relevant to nanocarbon synthesis, opening up other possibilities for nanosynthesis, particularly in resource-limited settings, educational venues, and the classroom itself.



## 1. Introduction

The carbon dot (C-dot), the latest nanoscale carbon and cousin to the fullerenes, graphenes, nanotubes, nanodiamonds and nanoonions, has recently emerged as a promising fluorescent nanomaterial that offers attractive, tunable, and eco-friendly properties (e.g., biocompatibility, inertness, low cytotoxicity) [1–3], in comparison to conventional quantum dots made from semiconductor materials such as CdX (X = S, Se, Te). Due to these appealing properties, research exploring various synthetic pathways employing a wide array of means and a wealth of carbon sources has recently witnessed an explosion. These synthetic approaches are generally lumped into two categories: top-down versus bottom-up approaches. Top-down approaches, examples of which include arc discharge [4], laser ablation [5], and electrochemical oxidation [6–8], involve the cleavage of macroscale carbon sources into smaller carbon "bits", eventually reaching nanoscale dimensions (i.e., C-dots). On the contrary, bottom-up approaches, such as thermal combustion [9,10], templated synthesis [11], microwave synthesis [12], and hydrothermal techniques [13], consist of assembling C-dots, essentially in an atom-by-atom or molecule-by-molecule manner, from carbon-containing molecular precursors. Despite the potentially green nature of C-dots, a substantial portion of these historical synthetic approaches involves the application of high temperatures, acidic/alkaline conditions, expensive (unsustainable) precursors, and/or extensive pre- and post-treatments that do not embrace the principles of green chemistry. Due to these shortcomings, low temperature thermal and hydrothermal approaches using sustainable carbon sources (including low- and negatively-valued wastes, an extreme example of which is human urine [14]) as well as syntheses that do not require ensuing functionalization steps have been developed [15–19]. For example, the use of a commercial induction coil heater for the low-temperature thermal synthesis of highly fluorescent C-dots was recently presented [20]. Hydrothermal carbonization in particular has been applied to a wide range of plant-derived wastes such as spent coffee grounds [21], pomelo peel [22], grass [23], willow bark [24], sweet potatoes [25], giant knotweed rhizome [26], orange juice [27],

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sweet pepper [28], and waste paper [29], all reported to generate C-dots. While these approaches are substantially greener than many earlier approaches, hydrothermal treatments do require specialized apparatuses (minimally, a Teflon-lined Parr™ bomb in a programmable oven) and are not easily scaled up. Consequently, approaches to the large-volume batch synthesis of C-dots using sustainable strategies remain highly desired.

Essentially a large-scale hydrothermal reactor, albeit with lower temperature and pressure limits, a domestic electric pressure cooker is an intriguing vessel for the simple, cheap, and economical production of nanomaterials. Previously, domestic pressure cookers were shown to be useful for the synthesis of inorganic nanomaterials such as PbS and CdS nanoparticles [30] and Cu–In–S/ZnS core/shell quantum dots [31]. To date, however, there has been no similar demonstration of the utility of a household pressure to prepare nanocarbons. As a proof of concept, the current work adds significantly to the scope of this utility by describing the first implementation of a domestic electric pressure cooker as a facile, economical, one-pot hydrothermal reactor for the batch synthesis of fluorescent nanoscale C-dots. Scheme 1 presents an overview of the pressure cooker synthesis employed in this work. The resulting hydrophilic C-dots possess photophysical properties akin to previously-reported C-dots, including excitation wavelength-dependent fluorescence. As we will show, the pressure cooker-synthesized C-dots function as useful, non-toxic nanoscale labels and sensitive nanoprobes in cellular imaging applications and for the quenchometric sensing of pertinent heavy metal ion contaminants such as $Cu^{2+}$. A distinct outcome of this research is that it allows those in resource-limited settings to contribute meaningfully to the development of novel nanocarbons, including carbon dots, without incurring significant startup costs. For instance, the pressure cooker employed here was purchased from a local department store for under US$100. In contrast, the required equipment for performing a standard hydrothermal reaction (i.e., stainless steel Parr™ bomb with PTFE cups and a programmable oven) will incur a cost of at least US$3000, and often significantly more.


**Scheme 1.** A domestic electric pressure cooker operating as a hydrothermal reactor for the synthesis of C-dots. The C-dots were synthesized by treating the precursors for twenty consecutive 99-min cycles under the cooker's "high pressure" setting. (No specific endorsement is implied or intended by the use of this particular brand of pressure cooker.)

## 2. Experimental section

### 2.1. Materials and reagents

All experiments were carried out using Ultrapure Millipore water (18.2 MΩ · cm). Citric acid monohydrate (≥99.5%), D(+)-glucosamine hydrochloride (>99%), urea (≥99.5%), sulforhodamine B (SRB), fetal bovine serum, cell culture media, phosphate buffer solution (PBS), trichloroacetic acid, acetic acid, potassium bromide (KBr, anhydrous, 99.95% trace metals basis), the chloride salts of $Ni^{2+}$ (98%), $Hg^{2+}$ (*ACS* > 99.5%), $Sn^{2+}$ (≥99.995% trace metal basis), and $Mn^{2+}$ (99.99% trace metals basis), and the sulfate salt of $Cu^{2+}$ (≥98.0%) were all purchased from Sigma–Aldrich (St. Louis, MO). Polyethylenimine (PEI), both 1.2 kDa (99%) and 10 kDa (99%), was purchased from Polysciences, Inc. The 96-well plates and the chloride salts of $Cu^{2+}$ (lab grade), $Fe^{3+}$ (ACS 97%–102%), $Sr^{2+}$ (99+% ACS), $Ba^{2+}$ (>99%), and $Ca^{2+}$ (99.999%) were obtained from Fisher Scientific (Pittsburg, PA). The anhydrous chloride salt of $Zn^{2+}$ (99.95% metals basis) was acquired from Alfa Aesar (Ward Hill, MA). All chemicals were used as received. Dialysis tubing (132 105, Spectra/Por 7, 1 kDa molecular weight cut-off, MWCO) was purchased from Spectrum Labs. The electric pressure cooker (Cuisinart model #CPC-600, 6 qt. capacity) employed in this work was purchased from a local department store. Mice embryonic fibroblast (MEF) cells were acquired from colleagues within the Dalton Cardiovascular Research Center.

### 2.2. Instrumentation

Absorbance spectra and fluorescence data were collected using a Cary Bio 50 UV–Vis spectrophotometer and a Varian Cary Eclipse Fluorometer, respectively. Fourier-transform infrared spectra were acquired on a Thermo-Nicolet Nexus 670 ESP FT-IR spectrophotometer using KBr pellets. Transmission electron microscopy (TEM) studies were conducted on carbon coated copper grids (Ted Pella, Inc. 01822-F, support films, ultrathin carbon type-A, 400 mesh copper grid) using a FEI Tecnai (F30 G2, Twin) microscope operated at a 300 keV accelerating voltage. Cells were observed and photographed using an inverted microscope Olympus X-71 with Normanski and fluorescence optics using 4, 10, 20 and 40x lenses and a black and white (Qimaging Retiga EXi) or color (Axiocam MRc5, Carl Zeiss) camera.

### 2.3. Synthesis of carbon dots (C-dots)

For the hydrothermal pressure cooker synthesis of C-dots, citric acid (CA) and glucosamine (GA) were selected as carbon sources, while polyethylenimine (PEI) and urea (U) were employed as N-doping/passivating agents. These precursors were chosen for several reasons: (1) they are benign and sustainable; (2) they are commercially available in pure form; (3) they are inexpensive; and (4) they contain carboxyl, hydroxyl, and amine functionalities expected to produce highly water-soluble carbon dots. The carboxyl/hydroxyl and amine components are essential as the pressure and temperature conditions within the pressure cooker vessel do not reach a critical level to decompose the carbon precursors but instead engage Maillard-like condensation/amination reactions to generate N-doped C-dots. With this in mind, the following precursor combinations were reacted in our pressure cooker: CA +10 kDa PEI, CA +1.2 kDa PEI, and CA + urea. The resulting products are