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Invited Article

Quick synthesis of 2-propanol derived fluorescent carbon dots for bioimaging applications

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ABSTRACT

Herein, for the first time, we present a one-pot ingenious preparative method for fluorescent carbon dots from 2-propanol (2P-CDs) without external treatments. Structure, morphology, chemical composition and fluorescence properties of the 2P-CDs were examined. These results confirm that the as-synthesized 2P-CDs are amorphous, monodispersed, spherical and the average particle size is 2.5 ± 0.7 nm. Most importantly, excitation-dependent emission properties were observed, which suggest that these 2P-CDs may be used in multicolor bioimaging applications. When incubated with HeLa cells, the 2P-CDs exhibit low cytotoxicity, and positive biocompatibility. Confocal microscopy image shows the uptake of 2P-CDs by HeLa cells and the application of probable biomarker is demonstrated.

1. Introduction

In this decade, luminous nanomaterials have many interested applications in biological screening, chemical sensing, and other related fields. Fluorescent carbon nanomaterials, mainly carbon dots, carbon nanoparticles and graphene quantum dots generate extensive attention for a large array of promising applications. Based on the carbon skeleton structure, typically exist in the range of less than 10 nm particles are known as carbon dots (CDs). Recently, carbon dots usually termed as quasi-spherical zero-dimensional nanomaterials, have shown peculiar potentials in various fields due to their optical properties, considerable biocompatibility, low toxicity, and photostability as well [1–3]. But, the metal-based semiconductor quantum dots cause serious health and environmental effects [4].

To date, copious sources worn to prepare CDs, pooled with top-down and bottom-up methodologies [5,6]. The top-down methods prepare CDs commencing larger carbon materials, such as nanodiamonds [7], graphite [8–11], carbon nanotubes [12,13], carbon soots [14], activated carbon [15], graphite oxide [16], while the bottom-up approaches synthesize CQDs from molecular precursors such as citric acid [17], glucose [18,19], and resin [20]. As a result of CDs surface chemistry, which is typically rich in carboxylic acid, alcohol and amine functionalities, CDs are hydrophilic, making them highly compatible with aqueous chemistry. They are generally considered to be environmentally benign and widely investigated for several applications. So, CDs take infront as capable alternative in targeted drug delivery [21], bioimaging and biomedicine [22–26], sensors [27], electrocatalysis [28–30] and photocatalysis [31]. In 2013, extremely blue fluorescent CDs were successfully primed, with a quantum yield in an aqueous solution similar to semiconductor QDs, marking a significant advance in this area [32]. Since then, attempts have been made on manifold applications of CDs in biomedicine and optoelectronics such as drug delivery [33], photodynamic therapy (PDT) [34], light emitting diodes (LEDs) [35] and solar cells [36].

However, the above mentioned methods were typically engrossing expensive instruments, vast solvent medium and/or time unpreserved. Hence pass up this, currently researchers pay attention in valuable, reliable, easier and solvent-free methodologies to acquire a large range of CDs for novel applications. In this study, for the first time, we produce carbon dots from 2-propanol

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(2P-CDs) based on a one-pot ingenious preparative method. This self-heating, rapid carbonization provided oxygen-containing 2P-CDs. Significantly, the as-synthesized 2P-CDs have low toxicity, offers enlarged avenues for various applications in bioimaging and afar.

2. Experimental

2.1. Chemicals

2-propanol (C_3H_8O, 99%, Merck), diphosphorus pentoxide (P_2O_5, 97%, Loba), hydrogen peroxide (H_2O_2, 30%, Rankem) and sodium carbonate (Na_2CO_3, 99.5%, Rankem) were all used as received. Deionized water (conductivity 3.5 μΩ/cm^2, Aquoion TBD 100 water system) was used for the whole experiment.

2.2. Synthesis of 2P-CDs

Typically, 5 g of diphosphorus pentoxide (P_2O_5) was taken in a 100 ml beaker; to this 3 ml 2-propanol was added and mixed well. Light brownish glue was obtained; to this 0.3 ml of hydrogen peroxide was progressively added. Mixture color was instantly changed into dark brown and volume also expanded due to foaming by spontaneous heat formed about 180 °C during the reaction. In this, 2-propanol is carbon precursor due to its low carbonization temperature, diphosphorus pentoxide act as carbonizer and hydrogen peroxide act as vigorous carbonization initiator. The self-engendered bubbles were produced to remove the excessive heat and utilized as the templates to restrict the size of the 2P-CDs. After 15 min, the reaction mixture was diluted by dropwise addition of 20 ml water under simple shaking, the brownish yellow supernatant after centrifugation (15000 rpm, 30 min, Remi RM12C) was neutralized by adding Na_2CO_3. Finally, it was dialyzed against deionized water through dialysis membrane (cellulose ester dialysis membrane, 1 KD MWCO) for 3 days, affording purified 2P-CDs.

2.3. Instruments

Ultra-violet excitation spectra (Perkin Elmer Lambda 25-UV/Vis spectrometer), Fluorescence emission spectra (Perkin Elmer LS-45 Fluorescence Spectrometer), Fourier Transform Infrared (FT-IR) Spectra (KBr, 4000-200 cm^{-1}, Impact 400D Nicholet Spectrometer), Zeta potential (Zetasizer, Malvern), X-Ray Diffraction (Seifert, X-ray diffractometer Siemens D500 Spectrometer, $20° \leq 2\theta \leq 80°$, Cu Kα radiation at 35 kV and 25 mA), MicroRaman measurements (HR 800, Jobin–Yvon, 1800 grooves mm^{-1} holographic grating, He–Ne laser of 633 nm, focus ≈3 μm and depth resolution was 0.5 μm, output 5 mW), XPS measurements (Escalab 220i-XL, Thermo VG, U.K., Mg-K_α source (1253.6 eV), spectra acquired with 100 eV pass energy) Surface analysis (high resolution transmission electron microscope), Elemental analysis (Energy-dispersive X-ray spectroscopy) and Selected Area Electron Diffraction patterns (HRTEM, EDS and SAED, JEOL JEM 2100 operating at 200 kV, 200-mesh C-coated Cu grid, Gatan Orious CCD camera (2K× 2K) for image recording), were used to analyze the 2P-CDs.

2.4. Cell culture

HeLa cells were purchased from the American Type Culture Collection (ATCC). The culture medium for cells consisted of Dulbecco's modified Eagle's medium (DMEM, Grand Island) supplemented with 10% fetal bovine serum (FBS, Invitrogen, Grand Island, NY) and 1% antibiotics (Invitrogen, Grand Island, NY) in a standard incubator (5% CO_2 atmosphere at 30 °C).

2.5. In vitro cell viability assay

HeLa cells were cultured by means of a recognized protocol. HeLa cells were placed at a concentration of 1×10^5 per well on a 96-well flat-bottomed culture plate and incubated with various concentrations of 2P-CDs (30, 60, 90, 120 and 150 μg mL^{-1}) for 24 h at 37 °C by using 5% CO_2 in a humidified incubator. The cell viability was evaluated by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. The outcome is presented as a reduction in metabolic activity in percentage relative to the metabolic activity of control cells cultured in growth medium only (100%).

2.6. Confocal analysis

HeLa cells (1×10^4) were seeded into 4-well plates containing 25 mm diameter cover glass and cells were grown for 24 h at room temperature. Before treatment with 2P-CDs (20 μg mL^{-1}), the cells were incubated for 30 min at 4 °C. After 2 h incubation with 2P-CDs,

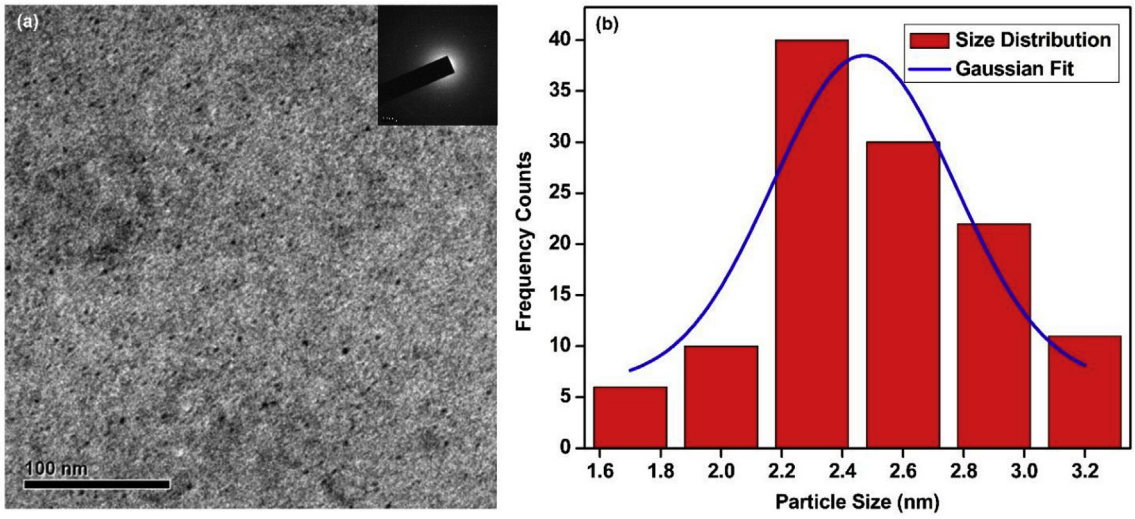

Fig. 1. Characterization of 2P-CDs: (a) TEM (inset: SAED pattern) and (b) Particle size distribution histogram.