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Eco-friendly synthesis of nitrogen-doped carbon nanodots from wool for multicolor cell imaging, patterning, and biosensing

Lihong Shi [a,*], Bo Zhao [a], Xiaofeng Li [b], Guomei Zhang [a], Yan Zhang [a], Chuan Dong [a], Shaomin Shuang [a]

[a] College of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China
[b] Taiyuan University, Taiyuan 030012, PR China

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ABSTRACT

We report an eco-friendly strategy for fabrication of nitrogen-doped carbon nanodots (N-CDs) and demonstrate their applications for multicolor cell imaging, patterning, and biosensing. N-CDs have been synthesized using wool as raw material via pyrolysis and microwave treatment, providing a green way for the production of N-CDs without the use of toxic/expensive solvents and starting materials. The prepared N-CDs exhibit exceptional advantages including high fluorescent quantum yield (22.5%), excellent biocompatibility, low toxicity, and satisfactory chemical stability. Depending on these superior properties, the N-CDs have been applied in multicolor bioimaging, patterning, and biosensing. Imaging of living cells has been observed with high resolution using N-CDs as a probe, which validates their use in imaging applications and their multicolor property in the living cell system. Additionally, the obtained N-CDs have been used as fluorescent inks for drawing luminescent patterns, showing favorable application in anti-counterfeit and optoelectronic dimensions. Most strikingly, the as-prepared N-CDs could visualize Fe^{3+} fluctuations in living cells with negligible autofluorescence based on their high sensitivity and selectivity detection for Fe^{3+} ions with a linear range of 0.1–10 μM and a detection limit of 10 nM.

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1. Introduction

Since their serendipitous discovery in 2004 [1] when researchers tried to purify carbon nanotubes by gel electrophoresis, carbon nanodots (CDs) have been magnificently transformed into nanolights. Typically, CDs are small discrete quasi-spherical nanoparticles with sizes less than 10 nm, displaying size and excitation wavelength dependent photoluminescence (PL) behavior. CDs offer a strong potential to replace traditional semiconductor quantum dots because of their superiority in unique luminescence performance, smaller size, high photostability against photobleaching and blinking, good biocompatibility, and low toxicity. These particular characters endow CDs enormous potential applications, such as bioimaging [2], sensing [3–5], photocatalysis [6], fluorescent ink [7], mimetics peroxidase [8] and energy conversion devices [9]. Currently, CDs are typically synthesized by two types of strategies: top-down and bottom-up routes. Top-down approaches involve laser ablation or electrochemical oxidation of graphite [10,11], electrochemical treatment of multiwalled carbon nanotubes [12], and chemical oxidation of commercially activated carbon [13]. Bottom-up methods include pyrolysis [14,15], wet oxidation [16,17], hydrothermal synthesis [18–21], and microwave assisted synthesis [18,22] with all sorts of carbon precursors.

Generally, CDs consist of three common elements: carbon, hydrogen and oxygen. In recent years, doped CDs have been a subject of topical interest in carbon nanomaterial research. Particularly, nitrogen-doped CDs (N-CDs) have been synthesized because nitrogen atoms have a comparable atomic size and five valence electrons available for bonding with carbon atoms [23]. The nitrogen bonding to carbon may cause disorder in the carbon hexagonal rings and create new luminescent centers by trapping the radiative electron-hole pairs, so that N-CDs showed distinctive optoelectronic, electrocatalytic, and luminescent features from their N-free counterparts [23–25]. During the past few years, efforts have been put into searching for ascendant methods or materials to prepare N-CDs, such as ultrasonic treatment of glucose and aqueous ammonia [26], annealing of graphene oxide under NH_3 [27], etc. Nevertheless, to the best of our knowledge, all these above-mentioned methods suffer from these drawbacks such as time-consuming, intricate processes, high cost and severe synthetic conditions, which limit

* Corresponding author.
E-mail address: shilihong@sxu.edu (L. Shi).

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their wide applications. Recently, N-CDs have been prepared from the natural materials, such as grass [28], soy milk [29], strawberry juice [30], soya beans [31], and milk [32]. Unfortunately, N-CDs synthesized from these cheap and abundant precursors failed to achieve high quantum yield (QY) (usually < 13%), causing difficulty for practical application. Therefore, the development of environmentally-friendly and cost-effective method for large scale synthesis of highly luminescent N-CDs remains challenging.

In this work, a green and economic strategy is developed for the synthesis of highly luminescent N-CDs with pyrolysis and microwave treatment using wool as a new carbon source. As-synthesized N-CDs show high fluorescent QY, excellent biocompatibility, low toxicity and satisfactory stability. Due to their favorable properties, the N-CDs have been successfully utilized to multicolor cell imaging, patterning, and biosensing.

2. Experimental

2.1. Materials

$AlCl_3$, $BaCl_2$, $CaCl_2$, $CdCl_2$, $CoCl_2$, $CuCl_2$, $FeCl_3$, $HgCl_2$, KCl, $MgCl_2$, $MnCl_2$, NaCl, $NiCl_2$, and $ZnCl_2$ were purchased from Beijing Chemical Corp. (Beijing, China). NaH_2PO_4 and Na_2HPO_4 were purchased from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Wool were form my domestic sheep (Shanxi, China). 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was obtained from Solarbio (Beijing, China). Distilled deionized (DDI) water was obtained from a Millipore Milli-Q-RO4 water purification system with a resistivity 18.2 MΩ cm^{-1} (Bedford, MA, USA). All the reagents were used as received without further purication. DDI water was used in experiments.

2.2. Synthesis and PL enhancement of N-CDs

N-CDs were synthesized by pyrolysis of wool. In a typical run, a crucible loaded with certain amounts of wool was transferred into a muffle furnace, and pyrolyzed at 300 °C for 2 h. After cooling down to room temperature, the black products were mechanically ground to fine powders. 0.5 g of the resultant sample was dispersed in 40 mL DDI water and magnetically stirred to form a black solution. The N-CDs aqueous solution was collected by removing larger particles through centrifugation at 4000 rpm for 15 min. Subsequently, N-CDs aqueous solution was subjected to dialysis for 12 h. PL enhancement of N-CDs was achieved by further microwave treatment. Typically, the obtained N-CDs aqueous solution was treated in a domestic microwave oven (700 W) for 6 min.

2.3. Characterization

Transmission electron microscopy (TEM) study was carried out in a JEOL JEM-2100 instrument operating at an accelerating voltage of 200 kV. Samples for TEM measurements were prepared by placing a drop of colloidal solution on carbon-coated copper grid and then dried at room temperature. The size distribution of N-CDs was performed by counting over 100 particles. Fluorescent photographs of N-CDs under UV light of 365 nm were operated with ZF-2 ultraviolet analyzer for three purposes from Shanghai City Anting electronic instrument factory. Fourier Transform infrared (FTIR) spectra were recorded on Bruker Tensor II spectrometer using a resolution of 4 cm^{-1}. The sample with 1 mg diluted by KBr (ratio 1:200) was pressed into the disc. Raman spectroscopy was characterized using Bruker Senterra dispersive Raman microscopy with laser wavelengths at 532 nm. X-ray photoelectron spectroscopy (XPS) data were obtained with an AXIS ULTRA DLD electron spectrometer from Shimadzu Company using 300 W Al Kα radiation. UV–vis absorption spectra were recorded on a Puxi TU-1901 UV–vis absorption spectrophotometer (China). Steady-state fluorescence measurements were performed on a Hitachi F-4500 spectrofluorometer (Tokyo, Japan). Fluorescence lifetime measurements were performed on an Edinburgh FLS920 spectrometer (Edinburgh, UK).

2.4. Fluorescence QY measurements

The relative fluorescence QY (Φ) of the N-CDs was calculated using the equation of $\Phi_x = \Phi_{std}\ I_x\ A_{std}\ \eta^2{}_x/(I_{std}\ A_x\ \eta^2{}_{std})$. The optical densities were measured on Puxi TU-1901 UV–vis absorption spectrophotometer. In the equation, I_x and I_{std} are the fluorescence intensities of the N-CDs and the standard, respectively. A_x and A_{std} denote the optical densities (OD) of the N-CDs and the standard, respectively. Quinine sulfate in 0.1 M H_2SO_4 was chosen as a standard with a QY of 0.54 at 360 nm. η_x and η_{std} denote the refractive index of the N-CDs and the standard, respectively. The absorbencies of all the samples in 1.0 cm cuvette were kept under 0.1 at the excitation wavelength to minimize re-absorption effects.

2.5. MTT assay

For the cell cytotoxicity text, human cervical carcinoma (HeLa) cells were first plated on a Costar 96-well tissue-culture cluster and cultured at 37 °C with 5% CO_2 in air for 3 h to adhere cells onto the surface. The well without cells and treatment with N-CDs was taken as a zero set. The medium was then changed with 100 μL of fresh DMEM supplemented with 10% FBS containing N-CDs, and the cells were allowed to grow for another 24 h. At least five parallel samples were performed in each group. Cells without treatment with N-CDs were taken as a control. After adding 20 μL of 5.0 mg mL^{-1} MTT reagent into every well, the cells were further incubated for 4 h, followed by removing the culture medium with MTT, and then 150 μL of DMSO was added. The resulting mixture was shaken for *ca.* 10 min at room temperature. The OD of the mixture was measured at 490 nm with a SunRisemicroplate reader (Tecan Austria GmbH, Grödig, Austria). The cell viability was estimated using the equation of $Cell\ Viability\ (\%) = (OD_{Treated}/OD_{Control}) \times 100\%$, where $OD_{Control}$ and $OD_{Treated}$ were obtained in the absence and presence of N-CDs, respectively.

2.6. Cell imaging

HeLa cells were cultured in DMEM supplemented with 10% FBS and incubated at 37 °C in a 5% CO_2 atmosphere. N-CDs aqueous solution (300 μL, 1.2 mg mL^{-1}) was added to the culture medium (1000 μL) at 0.3 mg mL^{-1} final concentration. After incubation for 0.5 h, HeLa cells were harvested using 0.25% trypsin/0.020% EDTA, washed three times (1.0 mL each) with pH 7.4 PBS (comprising 137 mM NaCl, 2.7 mM KCl, 8.0 mM Na_2HPO_4, and 2.0 mM KH_2PO_4), and kept in PBS for optical imaging by an Olympus FV1000 confocal microscope (Tokyo, Japan) with 40 × objective. Excited at 405 nm and 488 nm, blue emissions were collected using a 425–475 nm band-pass filter and green emissions were collected using a 500–540 nm band-pass filter.

2.7. Patterning

N-CDs solution (1.2 mg mL^{-1}) is encapsulated into the pen for drawing versatile fluorescent patterns at room temperature. Commercially available papers (the paper showed no background UV fluorescence) were chosen as the patterning paper. Photographs were taken using a UV light and multispectral fluorescence vivo molecular imaging system (S-0010A). Blue fluorescence patterns were obtained using UV light excitation (excitation: 365 nm; emission: 440 nm). Green fluorescence patterns were obtained using

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