Sensors and Actuators B 234 (2016) 15–20

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Solid phase reaction method for preparation of carbon dots and multi-purpose applications

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ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 17 April 2016
Accepted 20 April 2016
Available online 27 April 2016

Keywords:
CDs
Solid phase reaction method
Large scale
Probe
Fluorescent ink
Cell imaging

ABSTRACT

In this study, carbon dots (CDs) were first obtained by using solid phase reaction method (SPRM). Compared with other methods, SPRM shows remarkable advantages on simple, rapid, and large scale CDs' fabrication without post-treatment and solvent-free. In addition, the obtained CDs can be employed as ideal fluorescent Fe^{3+} probe and fluorescent ink. By taking advantage of its low-cytotoxicity, the CDs can be further applied in cell imaging successfully. This strategy offers a simple and efficient approach for preparing CDs in large-scale and lays a foundation for its further multi-purpose application.

1. Introduction

The emergence of 'zero-dimensional' carbon quantum dots (CDs) as a new nanomaterial has attracted intense interests due to its prominent features similar to traditional fluorescent dyes, such as high photostability [1], tunable emission [2], chemical inertness [3], and large two-photon excitation cross-sections [4,5]. In addition, CDs also exhibit special characteristics including low photo-bleaching, excellent water solubility, easy functionalization, low toxicity and good biocompatibility which make it become the most promising alternatives traditional semiconductor quantum dots (QDs) and organic dyes. Recently, cheaper carbon sources have been discovered [6–8]. Interestingly, Chen's group reported preparation of CDs by using eggs as precursor meaning that raw material problem has been solved for CDs large-scale production [9].

Since first discovered from purification of crude carbon nanotubes in 2004 [10], many efforts have been exerted on preparation of CDs. Up to now, many methods such as laser ablation [11], arc-discharge [10], electrochemical oxidation [12], acid oxydation [13], microwave heating [14–19], combustion/thermal [20–23] and supported routes [24] have been developed. However, problems including complex post-processes, high energy loss and so on still exist, which inevitably brings environmental pollution and resource waste. Therefore, developing the convenient, green, low energy loss and large scale fabrication of CDs is the urgent challenge in nanotechnology and nanochemistry. Until now, various solvents have been chosen as essential condition for preparing CDs in solution system. So, it is of great significance on developing a new method without solvent and complicated post-processing. Herein, we report a simple, low-cost, one-step solid phase reaction method (SPRM) for preparation new luminescent CDs without any solvent and post-processing. The obtained CDs can exhibit multi-purpose applications for highly selective probe for Fe^{3+}, fluorescence ink, and alive cells imaging.

2. Experimental

2.1. Materials and reagents

Citric acid (CA) was purchased from Shanghai Carbon Co., Ltd. (China). Other chemical solvents and reagents were of analytical reagent grade and were used without further purification. Deionized water was used to prepare all aqueous solutions. Inorganic salts $MnCl_2$, $CaCl_2$, $ZnCl_2$, $FeCl_2$, $NaNO_3$, KNO_3, $Co(NO_3)_2$, $Mg(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cd(NO_3)_2{\cdot}2H_2O$,

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http://dx.doi.org/10.1016/j.snb.2016.04.124
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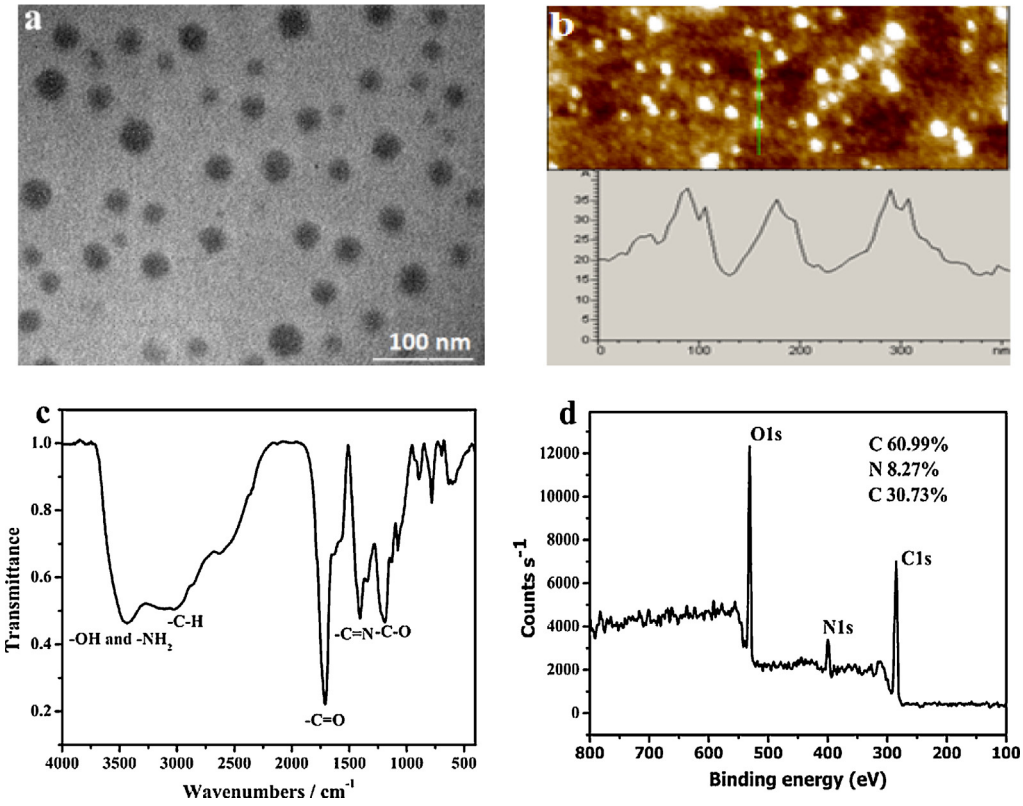

Fig. 1. (a) TEM, (b) AFM, (c) FT-IR, (d) XPS of CDs.

$NiNO_3{\cdot}6H_2O$, $AgNO_3$ and $(CH_3COO)_2Pb$ were dissolved in phosphate buffer (pH = 6.8) to obtain 20 μM aqueous solutions. Other chemicals were of analytical grade and used as received. All samples were prepared at room temperature and were shaken for 1 min before the test.

2.2. Apparatus

The size and morphology of CDs were observed by the transmission electron microscopy JEM-2100F (JEOL, Japan) and Atomic force microscope Agilent-5500 ILM (Agilent, USA). The potential was measured on a Nano-ZS90 zetasizer (Malvern, UK). X-ray diffraction (XRD) pattern of CDs was obtained using D/max 2500VL/PC (Japan) at a voltage of 40 kV and a current of 200 mA with 2 h scanning mode. Fourier transformed infrared (FTIR) spectra were acquired on Nicolet Nexus 670 Fourier transforms infrared (FT-IR) (Bruker, Germany). Ultraviolet–Visible (UV–vis) absorption spectra were measured using a Varian Cary 50 spectrophotometer (Varian, USA) with a 1 cm light path length. Fluorescence spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer (Varian, USA) with an excitation wavelength of 360 nm. Live cell imaging was performed using an inverted fluorescence microscope (Nikon eclipse, Japan). Raman spectrum was measured using a Labram HR800 (Jobin Yvon, French).

2.3. Synthesis of CA-Cl

A mixture of CA (0.5 g) and $SOCl_2$ (30 mL) were reacted in the presence of anhydrous DMF (0.5 mL) at 75 °C for 24 h under nitrogen atmosphere, and then excess $SOCl_2$ was removed by distillation, CA-Cl was obtained.

2.4. Synthesis of CDs

A mixture of 0.5 g CA-Cl and 0.5 g polyethyleneimine were placed in a 20 mL beaker and heated in an oven at 180 °C for 2 h. After cooling to room temperature, the yellow powder was obtained and stored in a dry cabinet for future use. The resulting CDs can show good solubility in H_2O, DMF, DMSO (Fig. S1, ESI†).

2.5. UV–vis and fluorescent experiments

CDs were dissolved in DMSO at an ambient temperature to obtain a stock solution (20.0 μM). The stock solution of metal ions was prepared in a phosphate buffer (pH = 6.8), and the concentration was 20.0 μM. Test solutions were prepared by placing 3 mL of the stock solution into a cuvette. All experiments were performed at room temperature.

2.6. MTT assay

HeLa cells were harvested (the cell density was adjusted to 10^5 cells per mL) and seeded in a 96-well plate (90 μL well^{-1}) overnight and CDs suspensions with different concentrations (20, 40, 60, 80, and 100 μg mL^{-1}) were then added. The cells were cultivated for 24 h, and 20 μL of 1 mg/mL MTT solution was then added to each cell well. After the cells were incubated for 4 h, the culture medium was discarded, and 150 μL of dimethylsulfoxide was added. The resulting mixture was shaken for 15 min in the dark at room temperature, and its optical density (OD) was measured by using a microplate reader (Thermo).

2.7. Cellular imaging

Human Hela cells were cultured in DMEM containing 10% fetal bovine serum in a humidified incubator at 37 °C and 5% CO_2. The