Chemical Engineering Journal 300 (2016) 75–82

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Facile synthesis of fluorescent graphene quantum dots from coffee grounds for bioimaging and sensing

Liang Wang [a], Weitao Li [a], Bin Wu [b], Zhen Li [c], Shilong Wang [b], Yuan Liu [a], Dengyu Pan [a,*], Minghong Wu [c,*]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, PR China
[b] School of Life Science and Technology, Tongji University, Shanghai 200092, PR China
[c] Shanghai Applied Radiation Institute, Shanghai University, Shanghai 200444, PR China

HIGHLIGHTS

- The highly fluorescent PEI-GQDs are synthesized from coffee grounds.
- The PEI-GQDs exhibit enhanced band-edge photoluminescence property.
- The PEI-GQDs serve as low-cytotoxicity biological imaging agents.
- The PEI-GQDs show high selectivity for detecting Fe^{3+} and Cu^{2+}.

ARTICLE INFO

Article history:
Received 31 January 2016
Received in revised form 15 April 2016
Accepted 22 April 2016
Available online 24 April 2016

Keywords:
Graphene quantum dots
Functionalization
Bioimaging
Sensing

ABSTRACT

We have developed a novel eco-friendly approach involving hydrazine hydrate-assisted hydrothermal cutting followed by functionalization with poly (ethylene imine) (PEI) for fabricating highly fluorescent graphene quantum dots from coffee grounds. The PEI-functionalized graphene quantum dots exhibit enhanced band-edge photoluminescence with single exponential decay. Their preliminary applications in bioimaging and sensing of heavy metals have been demonstrated.

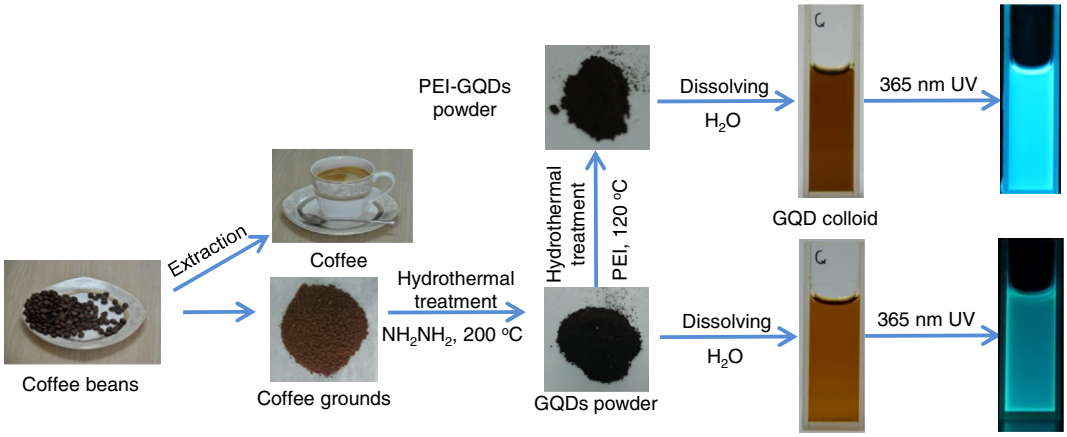
1. Introduction

Fluorescent nanomaterials have generated many applications in sensing [1,2], imaging [3–5], and optoelectronic devices [6,7] because of their unique optical properties. In past 20 years, efforts have been focused on the synthesis of semiconductor quantum dots (SQDs) with size-dependent emission wavelengths and high quantum yields (QYs) [8]. However, many of them were synthesized from toxic compounds such as CdX (X = S, Se, Te) and thus their large-scale applications would raise some potential environmental concerns [9]. Therefore, it is still in high demand to synthesize non-metal quantum dot materials for the above-mentioned applications. Compared with SQDs, graphene quantum dots (GQDs) possess their favorable attributes without incurring the burden of intrinsic toxicity [2,4,10–16]. As a consequence, a tremendous amount of researches has been devoted to the development of their applications in bioimaging [3,4,17–22], biosensing [23–25], light emitting diodes [26,27], solar cells [7,28], and photocatalysis [11,29]. It is thus of critical importance to exactly control their size (both diameter and layer number) and surface and edge chemistry during fabrication processes, because all these structural parameters will determine their electronic and optical properties associated with their various applications.

Towards this target, a lot of synthesis methods for various functionalized and non-functionalized GQDs have been established in recent five years [2–4,10–30]. Some involved chemical or electrochemical cutting using carbon precursors from nanocarbons (graphene sheets [31–33] and carbon nanotubes [34]) to bulk graphite [35] or counterparts such as artificial graphite [36,37], carbon fibers [38] and coal [39,40]. Apart from the top–down methods, a bottom–up strategy has also been developed using various aromatic molecules [41–44]. Some toxic organic small molecules have been employed to fabricate GQDs using multistep

* Corresponding authors.
E-mail addresses: dypan617@shu.edu.cn (D. Pan), mhwu@shu.edu.cn (M. Wu).

http://dx.doi.org/10.1016/j.cej.2016.04.123
1385-8947/



Scheme 1. Preparation procedures of GQDs and PEI-GQDs.

oxidative condensation reactions in organic solutions. In most cases, however, these organic synthetic methods suffer from some disadvantages, such as harsh reaction conditions, high prices, tedious processes, and the use of toxic starting materials [41–44]. In this regard, searching for precursors from regular food may provide green routes that could overcome the above mentioned drawbacks. On the other hand, some kinds of natural food have been consumed by human beings for centuries, and now are still very common in daily life. If natural food could be re-used as a non-toxic starting material for the synthesis of GQDs, such eco-friendly synthesis would be valuable. Recently there are few reports on fabricating fluorescent QDs from natural food such as rice husk [22], honey [45], glucose [46], milk [47], orange juice [48], due to their low cost, easy availability, and nearly unlimited resource. These results inspired us to further produce fluorescent GQDs from natural food. Despite instant coffee or coffee bean have been used to prepared fluorescent QD materials for cell-imaging [49,50], then there are low PL QYs limited their applications in many fields. Herein, we present a food route to fluorescent GQDs by cutting coffee grounds as the starting material without strong acid or expansive catalyst. The GQDs were further functionalized by poly (ethylene imine) (PEI). The functionalization is not only able to greatly enhance the fluorescence yield of GQDs, but also decreases the cytotoxicity of the GQDs at higher concentrations. The applications of PEI-functionalized GQDs (PEI-GQDs) for bioimaging and sensing are explored.

2. Experimental section

2.1. Preparation of GQDs and PEI-GQDs

Coffee beans were purchased from Zhongka® Coffee Food Co. Ltd. Hydrazine hydrate and microporous membrane (0.22 mm) were bought from Shanghai Chemical Reagent Co. Ltd. Poly (ethylene imine) was supplied by Alfar Aesar (1800, 30% w/v). The dialysis bag with retained molecular weight of 3500 Da was bought from Beijing Dingguo Changsheng Biotechnology Co. Ltd. Deionized water were produced using a Milli-Q system ($R > 18.1$ MΩ cm).

GQDs were prepared from used coffee grounds of coffee beans through a hydrothermal route. Firstly, coffee beans were crushed by grinder and changed to hot coffee through Philips® espresso machine. Used coffee grounds were cleaned and dried in an oven at 80 °C. In a typical procedure for synthesizing GQDs, 0.1 g coffee grounds and 1 ml hydrazine hydrate were dissolved into 10 ml water in an ultrasonic bath for 30 min. Then the solution was transferred into a 25 ml Teflon lined stainless autoclave. The sealed autoclave was heated to 150–200 °C in an electric oven and kept for additional 6–10 h. After cooled to room temperature, the product containing water-soluble GQDs was filtered through a 0.22 mm microporous membrane to remove insoluble carbon product, and further dialyzed in a dialysis bag for 2 days to remove unfused small molecules. The purified black GQDs were dried at 80 °C with a yield of 33%, and further used for structural characterization and property measurement. The synthetic procedure of PEI-GQDs was similar to that of the GQDs except for the addition of PEI in the media: A 10 ml GQD solution with the GQD concentrations of 800 mg L^{-1} was mixed with 0.1 g of branched PEI solution under magnetic stirring, and then transferred to a 25 ml Teflon lined stainless autoclave. After heated at 120 °C for 10 h, the suspension was cooled naturally to room temperature.

2.2. Structural characterization

Samples were characterized by AFM using a SPM-9600 atomic force microscope, TEM on a JEOL JEM-2010F electron microscope operating at 200 kV, X-ray powder diffraction (XRD) with a Rigaku D/max-2500 using Cu Ka radiation, FT-IR spectroscopy recorded on a Bio-Rad FTIR spectrometer FTS165, and Raman spectroscopy on a Renishaw in plus laser Raman spectrometer with 633 nm. Absorption and fluorescence spectra were recorded at room temperature on a Hitachi 3100 spectrophotometer and a Hitachi 7000 fluorescence spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) data were obtained with an AMICUS electron spectrometer from SHIMADZU using 300 W Al Kα radiation, and the binding energy calibrations were based on C 1s at 286 eV, N 1s at 400 eV and O 1s at 532 eV. The base pressure was about 3×10^{-9} mbar. The PL QY of GQD and PEI-GQDs aqueous solutions were determined by comparing the integrated PL intensities (excited at 370 and 390 nm respectively) and the absorbency values using 9,10-bis(phenylethynyl) anthracene in cyclohexane as the reference.

2.3. Cell imaging

Hela cells were cultured in Dulbecco's modified Eagle (DMEM) medium (Gibco, USA) with L-glutamine, penicillin/streptomycin (Gibco, USA), 10% (v/v) fetal bovine serum (Gibco, USA). Approximately 2×10^5 Hela cells were seeded in culture dishes (diameter: 40 mm) and cultured using the same culture medium (2 ml per dish) at 37 °C under 5% CO_2/95% air. All cells were incubated for at least 24 h until ~80% confluence was reached. A GQD aqueous solution was introduced to the cells with a final concentration of