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Microwave assisted one-step green synthesis of fluorescent carbon nanoparticles from ionic liquids and their application as novel fluorescence probe for quercetin determination

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ABSTRACT

In this study, a new sensitive and convenient method for the determination of quercetin based on the fluorescence quenching of fluorescent carbon nanoparticles (CNPs) was developed. The CNPs derived from ionic liquids were prepared using a green and rapid microwave-assisted synthetic approach for the first time. The one-step green preparation process is simple and effective, neither a strong acid solvent nor surface modification reagent is needed, which makes this approach very suitable for large-scale production. The prepared CNPs were characterized by high-resolution transmission electron microscopy, Fourier transform infrared spectrometry, elemental analysis and spectrofluorometry. In NH_3–NH_4Cl buffer solution (pH 9.47), the fluorescence signals of CNPs decreased obviously with increase of the quercetin concentration. The effect of other coexisting foreign substances on the intensity of CNPs showed a low interference response. Under the optimum conditions, the fluorescence intensity presented a linear response versus quercetin concentration according to the Stern–Volmer equation with an excellent 0.9989 correlation coefficient. The linearity ranged from 2.87×10^{-6} to 31.57×10^{-6} mol L^{-1} with the detection limit (3σ) of 9.88×10^{-8} mol L^{-1}. The recovery of this method was in the range of 93.3–105.1%. Therefore, the CNPs could to be a promising candidate as a fluorescence probe for the detection of trace levels of quercetin due to their advantages in low-cost production, low cytotoxicity, strong fluorescence and excellent biocompatibility.

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1. Introduction

Flavonoids, commonly found in fruits, vegetables and some beverages, represent a large group of plant phenols [1]. Flavonoids are derived from heterocyclic 2-phenylbenzopyrone. Commonly all the three cycles are substituted by hydroxyl groups or methoxy groups and discrete derivatives differ in the stage of substitution and oxidation [2]. Quercetin (Fig. 1) is a typical flavonol which is abundant in fruits and vegetables. During the past years, quercetin has drawn extensive attention as it displays a variety of biological activities including cardiovascular protection, anticancer activity, antiulcer effects, antiallergy activity, cataract prevention, antiviral activity and anti-inflammatory effects. Most of these beneficial effects were known due to the antioxidant activity of quercetin [3], thus it is of significance to develop an appropriate approach to detecting it. Hitherto, numerous analytical methods have been employed for the quantification of quercetin, such as high-performance liquid chromatography with UV absorption detector [4] or chemiluminescence detection [5], electrophoresis with a diode array detector [6] and electroanalytical methods [7,8]. Several fluorescence methods [9,10] have also been reported, which were considered to be the most promising methods due to their high sensitivity.

As novel fluorescence indicators, fluorescent semiconductor quantum dots (QDs) [11–16] have attracted considerable attention and could be widely used in biomedical and pharmaceutical analysis. However, heavy metals which are essential elements in these conventional semiconductors, are of restrictive use for concerns about their toxicity, stability and environmental hazards [17–19]. So how to fabricate benign nanomaterials with similar optical properties is an interesting challenge and have inspired intensive research efforts. In recent years, a new type of visible emitters have been reported exclusively based on fluorescent carbon nanoparticles (CNPs) [20–25]. They appear to be a promising alternative to traditional toxic metal-based semiconductor QDs in many fields due to their advantages in strong fluorescence, low cytotoxicity and excellent biocompatibility.

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Several methods of preparing eco-friendly fluorescent CDs or CNPs have been reported, and can be generally classified into two main groups: top-down and bottom–up methods [26]. The top-down method is to etch a larger carbon structure into individual nanoparticles, such as arc-discharge single-walled carbon nanotubes [27], laser ablation of graphite [20], electrochemical oxidation of graphite and multiwalled carbon nanotubes [28,29], carbonizing polymerized resols on silica spheres [30], chemical oxidation soots of candles, natural gas, commercially activated carbon and lampblack [31–33] and chemical oxidation of oxide graphene [34]. While the bottom–up method is to form nanoparticles from molecular precursors through chemical and thermal oxidation or microwave pyrolysis of carbonaceous compounds [25,35–39]. However, most of these synthesis methods involve expensive starting materials, great energy-consuming devices, intricate processes and the as-synthesized CDs or CNPs. Typically, the CDs or CNPs are always required to be oxidized by strong acid and further surface-passivated by surface modification reagent to improve the water solubility of these nanoparticles and modify the PL properties. Therefore, it is still a critical issue to design an economical, facile, effective and green synthetic route to produce strong fluorescent CDs or CNPs on a large scale.

Herein, we present an economical, facile, effective and green microwave pyrolysis approach to synthesize fluorescent CNPs. A characteristic feature of this one-step approach is that the formation and functionalization of CNPs are accomplished simultaneously through the microwave pyrolysis of the ionic liquids, neither a strong acid solvent nor surface modification reagent is needed. The synthetic process occurs in a domestic microwave oven using inexpensive ionic liquids as the necessary source of carbon which has the advantage of being relatively cheap and absolutely "green".

Recently, many methods for the determination of metallic ions, such as Hg^{2+}, Ag^{+}, Cd^{2+}, Fe^{2+}, Cu^{2+} and Pb^{2+} using fluorescent nanoparticles have been reported, which are based on the quenching or enhancement of the fluorescent intensity of the fluorescent nanoparticles. To broaden applicability of fluorescent nanoparticles in new areas, we explored a method based on the fluorescent quenching of CNPs by quercetin. In this study, we proposed a new kind of nanometer-sized fluorescent particles by a microwave-heating route. To the best of our knowledge, microwave assisted one-step green synthesis of CNPs derived from ionic liquids has not been reported so far. It was found that the fluorescence intensity of CNPs quenched in the presence of quercetin, and the quenched intensity of fluorescence was proportional to the concentration of quercetin. Based on this phenomenon, CNPs were employed as fluorescence probes for the determination of quercetin. This method was sensitive, rapid, accurate and simple, and could be used as a new and reliable means for the quantitative determination of therapeutic agents.

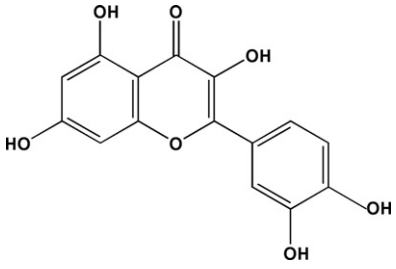


Fig. 1. Structure of quercetin.

2. Experimental

2.1. Apparatus

UV–vis absorption was characterized by a UV1800 UV–vis spectrophotometer (Shimadzu Corporation, Japan). Photoluminescence (PL) emission measurements were performed using a RF-5301PC fluorescence spectrophotometer (Shimadzu Corporation, Japan). The morphology of the as-synthesized nanoparticles was studied using a FEI Tecnai G2 F20 transmission electron microscope (TEM) and a IX71 inverted research microscope (Olympus, Japan). The surface groups on CNPs were measured with a 8400s FTIR spectrometer (Shimadzu Corporation, Japan). Elemental analysis was acquired with a Elementar Vario ELIII.

2.2. Materials and reagents

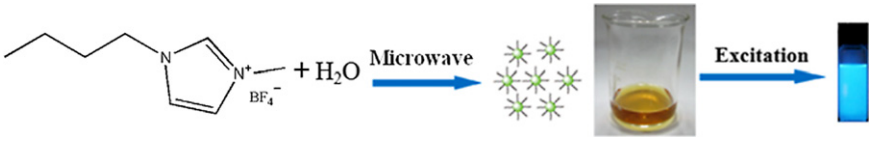
1-butyl-3-methylimidazolium tetrafluoroborate was purchased from Lanzhou Green hem ILS, LICP. CAS. China. Quercetin was purchased from shanghai China. All the chemicals were used as received without further purification.

2.3. Preparation of CNPs

As shown in Scheme 1, the fluorescent CNPs were prepared by a facile green route of microwave-assisted synthetic approach. In a typical synthesis, 0.5 g of 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$) was mixed with 20 mL of distilled water under stirring to form a clear transparent solution in a beaker. Then, the mixed solution was put into a domestic microwave oven (700 W) and heated for different time periods. The color-changed solution was centrifuged at 13,000 rpm for 30 min to remove less-fluorescent deposit. Finally, a clear yellow-brown aqueous solution containing CNPs was obtained.

2.4. Determination of quercetin

In a 10 mL volumetric flask was successively placed 10 μL of 3.69×10^{-6} mol L^{-1} CNPs and an appropriate volume of quercetin solution. The mixture was then diluted to the mark with NH_3–NH_4Cl buffer solution (0.10 mol L^{-1}, pH 9.47) and mixed thoroughly. The fluorescent spectra were obtained by scanning the emission from 300 to 800 nm on the spectrofluorimeter (with 5 and 5 nm slit width for excitation and emission, respectively), and F and F_0 which are the FL intensity of the CNPs at a given quercetin concentration and in a quercetin-free solution were measured at 354 nm.



Scheme 1. A schematic illustration of the preparation procedure of CNPs by microwave pyrolysis.

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