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Graphene quantum dots as additives in capillary electrophoresis for separation cinnamic acid and its derivatives

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ABSTRACT

A facile capillary electrophoresis (CE) method for the separation of cinnamic acid and its derivatives (3,4-dimethoxycinnamic acid, 4-methoxycinnamic acid, isoferulic acid, sinapic acid, cinnamic acid, ferulic acid, and trans-4-hydroxycinnamic acid) using graphene quantum dots (GQDs) as additives with direct ultraviolet (UV) detection is reported. GQDs were synthesized by chemical oxidization and further purified by a macroporous resin column to remove salts (Na_2SO_4 and $NaNO_3$) and other impurities. Transmission electron microscopy (TEM) indicated that GQDs have a relatively uniform particle size (2.3 nm). Taking into account the structural features of GQDs, cinnamic acid and its derivatives were adopted as model compounds to investigate whether GQDs can be used to improve CE separations. The separation performance of GQDs used as additives in CE was studied through variations of pH, concentration of the background electrolyte (BGE), and contents of GQDs. The results indicated that excellent separation can be achieved in less than 18 min, which is mainly attributed to the interaction between the analytes and GQDs, especially isoferulic acid, sinapic acid, and cinnamic acid.

During the past decades, with the discovery of C_{60}, carbon nanotubes, and most recently graphene, carbonaceous materials have received a great deal of interest [1]. In particular, graphene-based materials, consisting of two-dimensional single-atom carbon sheets, have been at the center of numerous investigations because of their outstanding physicochemical properties and widely used in various fields, including as molecular probing in living cells [2], a biosensor for electrochemical sensing [3], a pH sensor [4], a photovoltaic device [5], and a supercapacitor [6]. However, currently available graphene-based materials are produced by typical physical and chemical routes and are generally micrometer-sized graphene sheets [7].

Graphene quantum dots (GQDs), as a new type of quantum dot and rising star in the graphene family, are nanometer-sized graphene sheets and consist of a single layer or a few layers of carbon atoms in a closely packed honeycomb structure [8], with a size less than 100 nm, and provide π–π electrostatic stacking interaction and hydrogen bonding sites. Meanwhile, in comparison with micrometer-sized graphene sheets, GQDs have well-confined shapes, are well water soluble, and have ultrahigh surface area-to-volume ratios, yielding high loading capacities with analytes. Most important, the reduction in size of GQDs has initiated a few different properties such as quantum size effects, edge effects [9], and stable photoluminescence [10]. Based on the many outstanding properties of GQDs, we believe that GQDs could be one of the most attractive and promising separating materials in the analytical science fields such as capillary electrophoresis (CE), high-performance liquid chromatography (HPLC), gas chromatography

Abbreviations used: GQDs, graphene quantum dots; CE, capillary electrophoresis; HPLC, high-performance liquid chromatography; GC, gas chromatography; UV, ultraviolet; BGE, background electrolyte; NaOH, sodium hydroxide; H_2SO_4, sulfuric acid; HNO_3, nitric acid; HCl, hydrochloric acid; TEM, transmission electron microscopy; FTIR, Fourier transform infrared; LOD, limit of detection; EOF, electroosmotic flow.

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(GC), and solid phase microextraction (SPME). However, up to now, most experimental works on GQDs have been mainly focused on optical and imaging analysis fields [7,11,12], and there have been few reports on GQDs used as separating materials. As an attractive and powerful separation technique, CE is often chosen for the determination of analytes because of its potential for high separation efficiency, short migration time, and minimal reagent consumption [13,14]. To improve the efficiency of separation, the use of various materials (e.g., silica nanoparticles [15,16], carbon nanotubes [17], grapheme [18], single-wall carbon nanotubes [19], gold nanoparticles [20], β-cyclodextrin [21–23]) as additives is probably the simple way. This is because this method does not require any procedure for the immobilization of nanoparticles onto the capillary. Moreover, the amount of materials introduced into the capillary can be easily controlled, completely avoiding the problems associated with the poor reproducibility between different capillary columns [24,25]. Currently, many articles have reported that a variety of materials are used as additives for CE to study their separation mechanism, especially carbon-based materials. Valcárcel and coworkers used single-walled carbon nanohorns as additives for separation water-soluble vitamins in CE and obtained good separation [17]. Subsequently, they also used graphene nanoparticles as additives for improving the electrokinetic separation of nonsteroidal anti-inflammatory drugs. Based on the precedents of nanoparticles as powerful analytical tools in CE as additives and the above-mentioned excellent properties of GQDs, we believe that GQDs as additives in CE could exhibit great advantages, such as yielding high loading capacities with analytes, and GQDs introduced into the capillary could be easily fulfilled. To the best of our knowledge, there are few reports of work of CE separation using GQDs as additives.

To investigate the possibilities of their application in CE and the mechanism for improving analyte separation of GQDs, cinnamic acid and its derivatives (3,4-dimethoxycinnamic acid, 4-methoxycinnamic acid, isoferulic acid, sinapic acid, cinnamic acid, ferulic acid, and trans-4-hydroxycinnamic acid; structures are given in Fig. 1) were adopted as model compounds. This is mainly because these compounds, which have aromatic rings and hydrogen bonding sites, could interact with GQDs through π–π electrostatic stacking interaction, preferably having hydrogen bonding sites. In addition, these interactions could introduce changes in the electrophoretic velocity of the analytes and improve the selectivity of separation. Another reason is that these seven compounds have similar structures, and it was difficult to achieve good separation (especially isoferulic acid, sinapic acid, and cinnamic acid) by CE. Furthermore, these seven compounds widely existed in many traditional Chinese medicines, and they were not only important as stomachic, astringent, carminative, and antidiabetic agents but also displayed many pharmacological properties such as antioxidant, antimicrobial activity, and even prevention of cancer and possessed important clinical application value [26,27].

In this study, we successfully synthesized GQDs, which have a relatively uniform particle size with 2.3 nm by chemical oxidization and were further purified by a macroporous resin column to remove salts (Na_2SO_4 and $NaNO_3$) and other impurities. To research the possibilities of the application of GQDs in CE and develop the mechanism for improving separation efficiency of analytes, we report a simple CE method for the separation of cinnamic acid and its derivatives using GQDs as additives with direct ultraviolet (UV) detection. The separation performances of GQDs as additives in CE were studied through variation of pH, concentration of the background electrolyte (BGE), and contents of GQDs.

Materials and methods

Chemicals and reagents

All reagents used were of analytical grade unless otherwise stated. Graphite was purchased from Qingdao Nanshu Hongda Graphite Products (Qingdao, China). The macroporous resin was purchased from Sunresin New Materials (Xi'an, China). Sodium hydroxide (NaOH) was purchased from Sinopharm Chemical Reagent (Beijing, China). Sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) were purchased from Chengdu Kelong Chemical Reagent (Chengdu, China). HPLC-grade methanol (MeOH) was purchased from Shanghai First Reagent Factory (Shanghai,

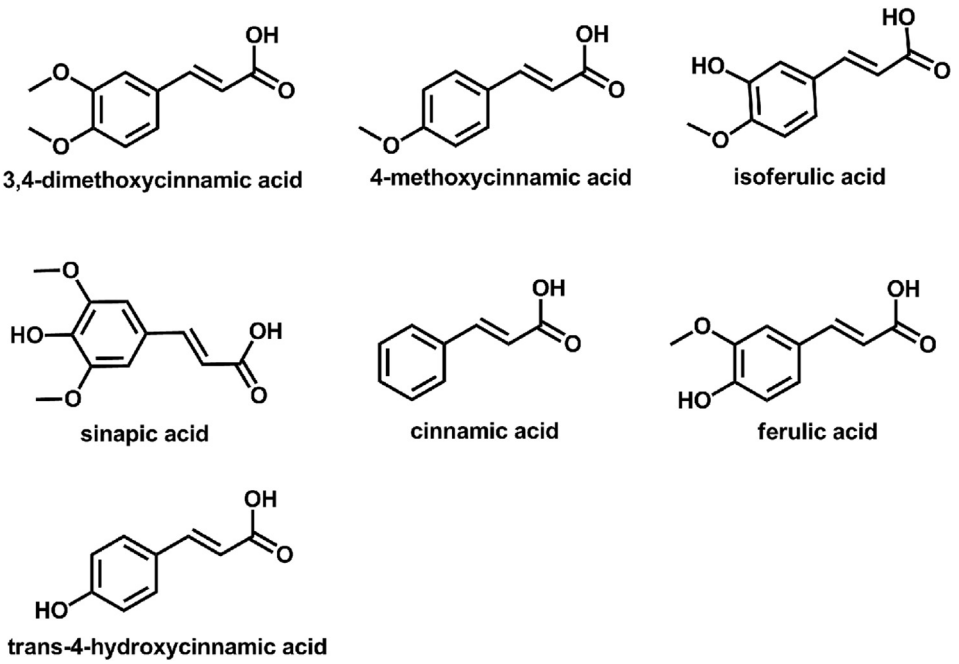

Fig.1. Chemical structures of cinnamic acid and its derivatives.