Fabrication of metal-organic frameworks and graphite oxide hybrid composites for solid-phase extraction and preconcentration of luteolin

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ABSTRACT

A novel solid-phase extraction sorbent, metal-organic frameworks and graphite oxide hybrid composite, was prepared by a solvothermal technique. The morphology and properties of the resultant material were examined by Fourier transform infrared spectroscopy, X-ray diffraction and field emission scanning electron microscopy. To evaluate the extraction performance of the resultant sorbent, luteolin was chosen as a model analyte. The extraction conditions were optimized. Based on these, a convenient and efficient solid-phase extraction procedure for the determination of luteolin was established and the subsequent quantification step was performed by square wave anodic stripping voltammetry. Under the optimal conditions, the oxidation current increased linearly with increasing the concentration of luteolin in the range of 5.0×10^{-9}–5.0×10^{-7} mol L^{-1} with a correlation coefficient of 0.9983 and a detection limit of 7.9×10^{-10} mol L^{-1}. The relative standard deviation of seven successive scans was 4.20% for 5.0×10^{-8} mol L^{-1} luteolin. This work not only proposes a useful method for sample pretreatment, but also reveals the great potential of metal-organic frameworks based hybrid materials as an excellent sorbent in solid-phase extraction.

1. Introduction

As one of the more common flavonoids, luteolin plays an important role in the human body. It is a frequent component of the human diet and has gained increasing interest because of its positive health effects. Luteolin has antioxidant, anti-inflammatory, anti-allergic, anticancer and immune-modulating properties to suppress hyperactive immune systems [1–3]. In clinic it is a promising agent for use in ophthalmology, cardiovascular disease, hepatitis, etc. Consequently, the development of reliable methods for the determination of luteolin is of particular significance.

So far, several methods have been investigated to determine trace amount of luteolin, such as gas chromatography [4], high-performance liquid chromatography [5] and capillary zone electrophoresis [6]. The determination of luteolin using these techniques shows high sensitivity, but they also requires expensive instruments, time-consuming pre-treatment steps, skilled operators and large quantity of organic solvents. Moreover, these techniques cannot be used for in situ assay. Electrochemical sensors show advantages of cheap instrument, simple operation and time-saving, and many electrochemical methods have been reported for luteolin sensor [7,8]. For instance, Wu et al. used a heated pencil lead disk electrode

to determine luteolin in simulated human urine [9]. Franzoi et al. constructed a electrochemical biosensor for luteolin based on silver or gold nanoparticles in ionic liquid and laccase immobilized in chitosan modified with cyanuric chloride [10]. Liu et al. depicted the determination of luteolin at a glassy carbon electrode (GCE) for pharmaceutical analysis [11].

Due to low concentrations of analytes and complexity of matrices, preconcentration is usually necessary before instrumental analysis. Some extraction methods, for example, liquid–liquid extraction [12], cloud point extraction [13], and solid-phase extraction (SPE) [14,15], have been employed to extract desired organic compounds from a sample matrix. Among these techniques, SPE offers an excellent alternative to the conventional sample preparation methods because of their simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor and sensitivity.

Metal-organic frameworks (MOFs), formed by coordination bonds between metal clusters and organic linkers, have shown significant potential for hydrogen storage, gas sorption and separation, and catalysis owing to their high specific surface areas and tunable pore sizes [16–18]. More efforts have been made to fabricate MOFs based hybrid composites for analytical applications, such as n-alkanes separation [19], lead ion sensing [20], polycyclic aromatic hydrocarbons extraction [21,22] and electrocatalytic oxidation [23]. Graphene is the most recent member of the multi-dimensional carbon-nanomaterial family. As one of the most important derivatives of graphene, graphene oxide (GO) has attracted significant

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attention as a precursor of chemically converted graphene because of the advantages of large surface area, excellent conductivity and strong mechanical strength. These properties made GO as a superior candidate for solid-phase extraction [24,25]. However, the combination of metal-organic frameworks with graphene oxide ($Cu_3(BTC)_2$/GO) as a selective sorbent has not been explored until now. The purpose of this study is to examine the feasibility of $Cu_3(BTC)_2$/GO hybrid composites for the application in solid-phase extraction. Luteolin was selected as a model analyte for its potential impact on human health. The factors influencing the efficiency of solid-phase extraction were systematically studied prior to its determination with square wave voltammetry. The proposed method was successfully applied to determine luteolin in real samples and satisfactory results were obtained.

2. Experimental

2.1. Instrumentations

Electrochemical measurements were carried out with a CHI 852C electrochemical workstation (Shanghai Chenhua Instrument Company, China). A three electrode-system, with glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the auxiliary electrode, were used in the measurements. All potentials were given with respect to the Ag/AgCl electrode. A Tensor 27 spectrometer (Bruker Co., Germany) was used to obtain Fourier transform infrared (FTIR) spectra. The scanning electron micrographs (SEM) images were obtained by scanning electron microscope (Hitachi S-4800, Japan). The crystalline materials were analyzed by X-ray diffraction (XRD) using a D8 Super Speed (Bruker AXS, Germany).

2.2. Reagents and materials

A 0.01 mol L^{-1} luteolin stock solution were prepared by dissolving 0.2862 g luteolin (Aladdin, Shanghai, China) in 100 mL 0.005 mol L^{-1} NaOH. Working standard solutions was obtained by step-wise dilution. Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), benzene-1,3,5-tricarboxylate (BTC), and N, N-dimethylformamide (DMF) used in this work were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless indicated otherwise. Phosphate buffer solution was prepared by mixing the stock solution of 0.1 mol L^{-1} NaH_2PO_4 and 0.1 mol L^{-1} Na_2HPO_4 and adjusting the pH with 0.1 mol L^{-1} H_3PO_4 or 0.1 mol L^{-1} NaOH. Graphite oxide was prepared using the Hummers method by graphite powder (Jinshan Chemicals, Shanghai, China) [26]. Double deionized water (18 MΩ cm) was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Preparation of $Cu_3(BTC)_2$/GO hybrid composites

$Cu_3(BTC)_2$/GO was synthesized according to a previous report after a minor modification [27]. Briefly, $Cu(NO_3)_2$ (10 g) and H_3BTC (5 g) were dissolved in DMF (85 mL), which was stirred and sonicated for 5 min. Then, ethanol (85 mL) and deionized water (85 mL) were added to the solution in turn with stirring for 5 and 30 min, respectively. After that, GO powder (consisted of 10 wt% of the final material weight) was added to the well-dissolved MOF precursors with sonicating the resulting mixture for 30 min. Finally, the mixture was then transferred to a round-bottom flask and heated at 85 °C in an oil bath for 21 h under shaking. After cooling to ambient temperature, the products were filtered and washed several times with sufficient volume of water and ethanol and then dried at 60 °C for 6 h before use. Moreover, $Cu_3(BTC)_2$

was also prepared according to the above-mentioned procedure without the adding of GO powder for comparative analysis.

2.4. Sample extraction and preconcentration procedure

The procedure for the solid-phase extraction is as follows: a portion of 10 mL sample solution containing analyte was transferred to a beaker; the pH value was adjusted to 6 with 1 mol L^{-1} HNO_3 or 1 mol L^{-1} NaOH. Then, 15 mg of sorbent was added, and the solution was stirred for 20 min to facilitate adsorption of the luteolin onto the sorbent. After the extraction, the suspension was separated and the sorbent was shaken with 2.5 mL ethanol and phosphate buffer solution mixture (pH=5). Finally, elution solvent was transferred into an electrochemical cell for subsequent detection by square wave voltammetry.

3. Results and discussion

3.1. Characterizations of the $Cu_3(BTC)_2$/GO hybrid composites

Fig. 1 exhibits the FTIR spectra of GO, $Cu_3(BTC)_2$ and $Cu_3(BTC)_2$/GO. For GO, the FTIR spectrum indicate the presence of C=O (1725 cm^{-1}), C–O (1052 cm^{-1}), C–O–C (1223 cm^{-1}) and C–OH (1428 cm^{-1}) in the GO samples. The peak at 1615 cm^{-1} is related to a resonance peak of C–C stretching and absorbed hydroxyl groups in the GO [28]. As for $Cu_3(BTC)_2$, the peaks at 1442 and 1371 cm^{-1} are attributed to the symmetric stretching of carboxylate group in the BTC linker. The peak appeared at 1442 cm^{-1} is produced by a combination of benzene ring stretching and deformation modes, and the peak around 700 cm^{-1} is related to bending vibration of C–H. The FTIR absorption band observed at 507 cm^{-1} is assigned to a vibrational mode directly involving the Cu center [29–31]. After GO incorporation, the high intensity $Cu_3(BTC)_2$ peak swamped the characteristic GO peak due to the rather small content of GO. Hence, the FTIR spectrum of $Cu_3(BTC)_2$/GO are similar to that of $Cu_3(BTC)_2$.

Fig. 2 shows the X-ray diffraction patterns of the samples GO, $Cu_3(BTC)_2$ and $Cu_3(BTC)_2$/GO. The GO spectrum was displayed at 2θ value of 12°, which suggests that the as-prepared GO has a high degree of orientation with an interlayer distance of 7.3 Å. The diffraction pattern of $Cu_3(BTC)_2$ is in agreement with those found for well-defined $Cu_3(BTC)_2$ crystals, indicating that the current material has the expected structure [32]. The XRD patterns of GO incorporated $Cu_3(BTC)_2$ showed the same diffraction patterns as of $Cu_3(BTC)_2$, confirming that GO incorporation did not disturb or destroy the $Cu_3(BTC)_2$ crystal structure. This phenomenon is
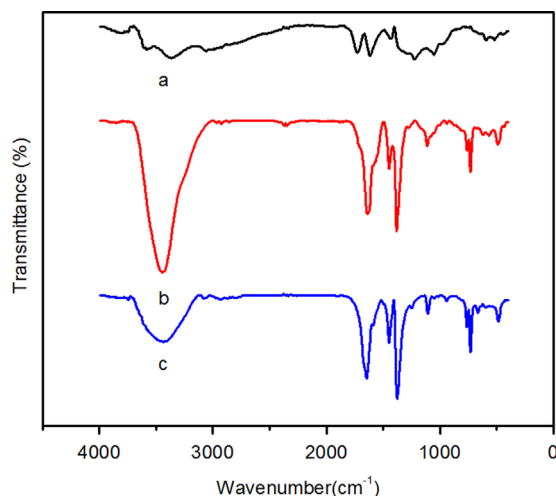

Fig. 1. FTIR spectra of (a) GO, (b) $Cu_3(BTC)_2$, and (c) $Cu_3(BTC)_2$/GO.