Journal of the Taiwan Institute of Chemical Engineers 84 (2018) 188–195

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Synthesis of hierarchical mesoporous graphite oxide/Al_2O_3 from MIL-100(Al) for the electrochemical determination of caffeic acid in red wine samples

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ARTICLE INFO

Article history:
Received 13 October 2017
Revised 26 December 2017
Accepted 3 January 2018
Available online 2 February 2018

Keywords:
Metal-organic frameworks
Graphitic porous materials
Cyclic voltammetry
Amperometry
Caffeic acid
Wine samples

ABSTRACT

We have synthesized the hierarchical mesoporous graphite oxide (HMGO) through simple single step carbonization method by using MIL-100(Al) metal-organic framework as a template. To study the influence of temperature in the synthesis of HMGO, various carbonization temperatures (700, 800, and 900 °C) were fixed without any additional carbon sources. The newly prepared HMGO showed uniform morphology, pore-size distribution centered on 10 nm with high surface area (370–470 m^2/g) and excellent electrochemical ability. Hence, we have constructed an amperometric sensor for the trace level detection of caffeic acid (CA) by using HMGO as a modifier in glassy carbon electrode (GCE). The good electro catalytic activity of HMGO film modified GCE can be explained from the low over potential and high redox peak current obtained toward the detection of CA. Our demonstrated sensor works in a wide linear range (0.01–608 µM) with low limits of detection (0.004 µM) and high sensitivity (429 $\mu A/mM/cm^2$). In addition, the selective determination of CA even in presence of other interfering molecules, reveals the good selectivity of HMGO/GCE. The commercially available wine samples were further utilized to demonstrate the practical feasibility of HMGO modified GCE. The acceptable values of stability, repeatability and reproducibility also support the practical applications of our fabricated electrode.

1. Introduction

Porous carbon materials (PCMs) have been considered as hopeful materials in the field of nanoscience and nanotechnology because of their high surface area, large pore size and volume and good electrochemical properties [1,2]. Remarkably, they have been displayed as good electro catalysts in the field of electrochemical sensors, biosensors, fuel cells and supercapacitors [3–6]. Although there are several synthetic methods available for the preparation of porous carbon materials, the single step synthesis of porous carbon materials from metal-organic frameworks (MOFs) have gained more attention in recent years. The properties such as exceptional surface area and controlled pore textures have highly attracted the researchers to synthesize MOFs derived carbon materials. Crystallinity and nanopores of MOFs can be easily controlled by suitable metal and linkers. To date, many studies have been reported for the transformation of MOFs of various topologies with/without additional carbon sources into porous carbons having high surface area through direct carbonization process under an inert atmosphere [7,8]. Nevertheless, the direct carbonization of MOFs to porous carbon without additional carbon source is more preferable because of its single step method. In the carbonization process, the MOF crystals are converted into bulk carbon powder at high temperature, which will result in reduced effective special surface area. Interestingly, the morphology of obtained MOFs derived carbon will be similar to the morphology of original MOFs at controlled temperature carbonization [6–8]. However, the obtained carbon materials usually have a low graphitic degree. Therefore, a great deal of research investigation has been devoted to the synthesis of carbon materials with retention of their original MOF morphology [9].

On the other hand, caffeic acid (3,4-dihydroxycinnamic acid) represents the secondary metabolites which are the naturally occurring phenolic acids (group of phenolic compounds) in citrus fruits, apples, berries, olive oil, coffee, wine and certain vegetables

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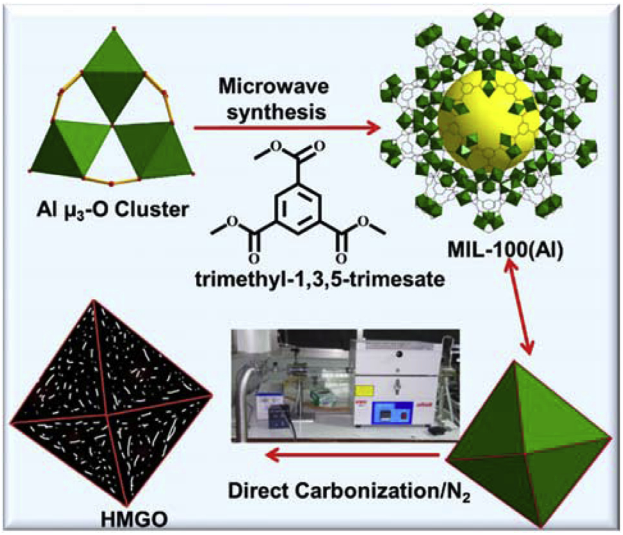
https://doi.org/10.1016/j.jtice.2018.01.006



Scheme 1. Schematic representation for the preparation of hierarchical mesoporous graphite oxide.

such as broccoli, onion, soy-beans and lettuce [10,11]. The significant features of caffeic acid (CA) have been widely studied in the areas of medicine and biochemistry. Remarkably, the biologically important properties including anti-oxidant against cardio-vascular diseases, anti-inflammatory, anti-carcinogenic and immuno-regulator have motivated the present-day researchers to focus on the sensitive determination of CA [12,13]. Relative to other conventional methods namely chromatography [14] and capillary electrophoresis [15], electrochemical method of CA detection has received more attention due to its simplicity, low cost, high sensitivity and selectivity. In general, the conventional electrodes with a pronounced fouling effect showed some disadvantages such as poor reproducibility, selectivity and low sensitivity in the determination of CA [16]. Hence, many new materials such as polymers [17], nanoparticles, molecularly imprinted siloxanes [12] and carbon materials [16,18] have been used as modifiers in electrodes to overcome these problems. Among these materials, carbon based materials have attracted the researcher's attention because of their low cost and good electrocatalytic properties.

Since the porous carbons from MOFs have received the recent attention to build up sensitive and reliable electrochemical sensors and biosensors, few reports dealing about the porous carbon derived from MOF for the electrochemical sensing applications have been reported. For example, Chen and co-workers prepared nitrogen doped porous carbon from direct carbonization of ZIF-8 MOF for electrochemical sensing of ascorbic acid, dopamine and uric acid [19]. To our knowledge, the reports of direct carbonized MOF materials as electrochemical sensors have been limited till date. With this above background, we have prepared hierarchical mesoporous carbon (HMGO) through direct carbonization of MIL-100(Al) without using any additional carbon source under N_2 atmosphere (Scheme 1). Considering the fact that, the pore texture of the resultant carbon material is crucially determined by the morphology and pore characteristics of the template, the MIL-100(Al) template led to a larger proportion of mesopores in the resultant graphite oxide materials. With uniform morphology, mesopores distribution and excellent electrochemical properties, the newly synthesized HMGO materials were used to modify a glassy carbon electrode (GCE). Furthermore, we have evaluated the analytical performance of HMGO/GCE for the determination of CA in commercial wine samples. Our fabricated HMGO/GCE shows good sensitivity, wide linear range and practical feasibility toward the detection of CA.

2. Experimental section

2.1. Chemicals

Caffeic acid, and all the other chemicals were purchased from Sigma–Aldrich at an analytical grade. 0.05 M phosphate buffer solution (PBS) was prepared with sodium dihydrogen phosphate and sodium phosphate dibasic (NaH_2PO_4 and Na_2HPO_4) and used as a supporting electrolyte for the entire electrochemical studies. Prior to each experiment, all the solutions were deoxygenated with prepurified N_2 gas for 15 min unless otherwise specified. All the electrochemical experiments were done by using double distilled water (conductivity ≥ 18 MΩ cm).

2.2. Characterization

The phase purity of all the compounds was examined by powder X-ray diffraction (PXRD) using a Bruker D8 PHASER instrument. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} with a JASCO FT/IR-460 spectrophotometer using KBr pellets. Raman spectra were recorded on a CCD detector (Jobin Yvon, Symphony series 1024 × 256 pixels) using an He–Ne laser with an excitation wavelength of 632.8 nm. The N_2 gas sorption isotherms were measured at 77 K using ASAP 2020 system of Micrometrics. Ultrahigh purity grade N_2, and He were used as received. Before the gas sorption measurements, the sample was initially dehydrated at 423 K for 24 h under vacuum. Scanning electron microscopy (SEM, using a JEOL JEM-7600F instrument) and transmission electron microscopy (TEM, using a JEM-2010 instrument) were employed to characterize the morphology. Electrochemical studies were performed using CHI 6171D work station in a conventional three electrode system with modified GCE of area 0.071 cm^2 as working electrode, saturated Ag|AgCl (saturated KCl) as reference electrode and Pt wire as counter electrode. Amperometric measurements were taken by using analytical rotator AFMSRX (PINE instruments, USA) and rotating disc glassy carbon electrode (RDE, area 0.21 cm^2)

2.2.1. Synthesis of MIL-100(Al)

MIL-100(Al) MOF was synthesized by following the prepublished procedure [20] with small modification. A mixture of $Al(NO_3)_3{\cdot}9H_2O$ (0.664 g), trimethyl-1,3,5-trimesate (0.3783 g), HNO_3 (1 M, 0.3 mL) and deionized water (5.0 mL) were taken in a 100 mL Teflon-liner autoclave and positioned in a microwave hydrothermal reactor, and the temperature profile was set. The reactor was heated from 25 to 200 °C within 25 min, maintained for 30 min and then cooled to 25 °C in 28 min. The resulting yellow powder was filtered and washed with distilled water for several times. It was purified by using DMF (at 150 °C for 4 h) and water (at 80 °C for 24 h). The resulting white solid was carefully centrifuged and washed with hot water for several times. Finally it was dried overnight at 80 °C in an oven. The as-synthesized MIL-100(Al) sample was activated at 120 °C for 12 h under vacuum for further characterizations and applications.

2.2.2. Synthesis of hierarchical mesoporous graphite oxide (HMGO)

The HMGO materials were synthesized by simple one-step direct carbonization method with activated MIL-100(Al) as the only precursor. The activated MIL-100(Al) (0.400 g) was taken in a silica boat and placed in a furnace chamber. Before heating, the chamber was evacuated and then N_2 atmosphere was created by passing N_2 gas in to the chamber for 1 h. Then, the carbonization was started from room temperature to high temperature (700, 800 and 900 °C) under N_2 atmosphere with a heating rate of 5 °C/min,