Journal of Electroanalytical Chemistry 818 (2018) 149–156

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Nanoporous carbon derived from dandelion pappus as an enhanced electrode material with low cost for amperometric detection of tryptophan

Junfeng Han[a,b], Jing Zhao[a], Zixiang Li[b], Hongquan Zhang[a], Yongde Yan[a,*], Dianxue Cao[a], Guiling Wang[a,*]

[a] Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin, Engineering University, Harbin 150001, China

[b] College of Chemistry and Chemical Engineering, Mudanjiang Normal University, Mudanjiang 157011, China

ARTICLE INFO

Keywords:
Nanoporous carbon
Electrocatalytic oxidation
Amperometry
Tryptophan
Biomass

ABSTRACT

A new type of nanoporous carbon (NPC) was synthesized using dandelion pappus as a cost-effective carbon source through chemical activation with phosphoric acid. Notably, NPC is first considered to be used as an enhanced electrode material for the analysis of tryptophan (Trp). The high electrical conductivity of nanoporous carbon modified electrode (NPC/GCE) was better demonstrated by cyclic voltammetry using the ferricyanide system as a probe. Furthermore, the NPC/GCE exhibited an excellent electrocatalytic activity toward Trp oxidation with a decreased overpotential and improved current response, mainly due to the porous structure and large specific surface of nanoporous carbon. The electrocatalytic oxidation mechanism of Trp at the modified electrode was also investigated by cyclic voltammetry. The amperometric response of NPC-based sensor is linear in the 1 μM to 103 μM concentration range and the sensitivity is 171.43 μA mM^{-1} cm^{-2}. The proposed sensor was also successfully applied to the determination of Trp in real samples, and the satisfactory recoveries were obtained.

1. Introduction

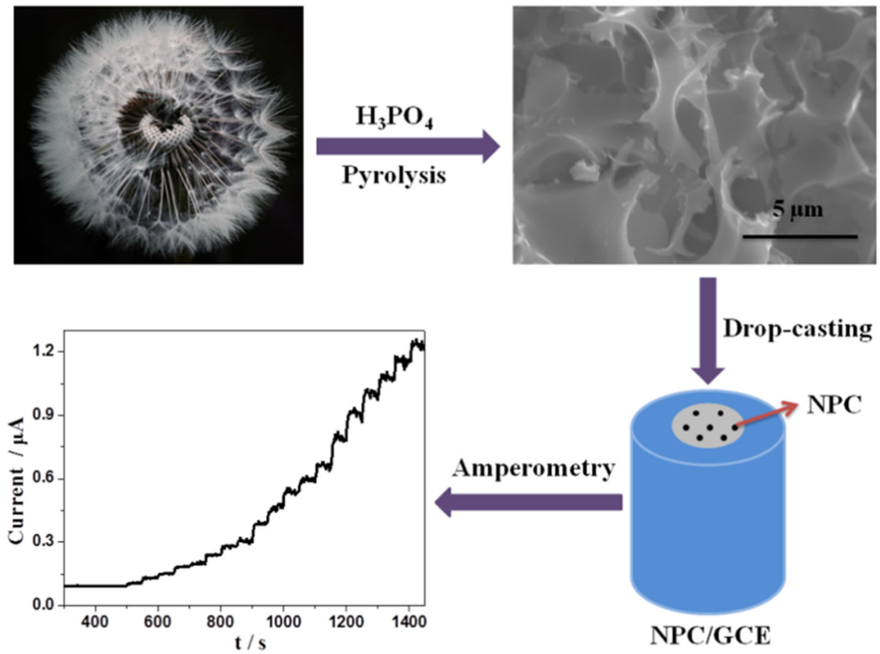
As an important essential amino acid, tryptophan has a crucial role in the metabolism of human body. Apart from synthesizing protein for body growth, it is a precursor for serotonin, niacin and melatonin [1]. An appropriate level of tryptophan intake prevents and treats certain diseases such as Alzheimer's disease, heart disease, psychotic depression, schizophrenia and hepatic disease [2–5]. Thus, the detection of tryptophan is significantly important for the development of medicine technology.

Although high-performance liquid chromatography [6], fluorimetry [7], chemiluminescence [8] and capillary electrophoresis [9] could be used to monitor Trp, but they are expensive, complex and time-consuming. Recently, electrochemical technique has attracted great interest in the field of tryptophan analysis due to its high sensitivity, easy operation and low-cost. However, the direct electro-oxidation of Trp usually requires a high overpotential at bare electrodes, leading to electrode fouling, poor sensitivity and low selectivity [10]. Various substances, such as MWNTs [11], carbon nanofibers [12], β-CD-MNPs [13], AuNPs-PARS [14] and Ag@C core-shell nanocomposite [15], have been applied to modify the electrode surface exhibiting better analytical performances. All of these contributions manifest that the electrochemical response of analytes depends very much on the microstructure and surface properties of working electrode. Thus, interest continues in the design of new modifier with novel structures and properties for tryptophan analysis.

Biomass-derived nanomaterials have provoked considerable interest in electrochemistry due to their large specific surface, high electrical conductivity, good chemical stability and low cost. And they have been applied in various fields, such as energy storage [16–19], catalyst [20] and analysis [21,22]. Other than being an ingredient of herbal tea, salad or wine, dandelion is pretty useless plant. Fortunately, the dandelion pappus possesses the hollow and thin-walled structure. It has been proven that the biomass with hollow and multilayer morphology can be used as an ideal precursor for advanced nanomaterials [16,23]. In this work, we developed a simple, rapid protocol for synthesizing nanoporous carbon using dandelion pappus as cost-effective precursor. The morphological and chemical characteristics confirmed that the obtained sample possesses the highly porous structure and large specific surface area. Then, we employed as-prepared nanoporous carbon as an enhanced electrochemical sensing element for the determination of Trp (Scheme 1). Cyclic voltammetry showed that the nanoporous carbon

* Corresponding authors.
E-mail address: wangguiling@hrbeu.edu.cn (G. Wang).

https://doi.org/10.1016/j.jelechem.2018.04.044
Received 27 December 2017; Received in revised form 18 April 2018; Accepted 19 April 2018
Available online 21 April 2018
1572-6657/



Scheme 1. Illustration of the preparation of NPC/GCE for Trp determination.

modified electrode could catalyze the electrochemical reaction of Trp, resulting in a lower oxidation potential (0.606 V) and higher current response (12.78 μA). The amperometry study showed a wide linear range of 1–103 μM with a low detection limit of 30 nM (S/N = 3). Moreover, the proposed sensor based on NPC was successfully used for the determination of Trp in practical samples.

2. Experimental

2.1. Materials and reagents

Tryptophan, phosphoric acid and other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (http://www.sinoreagent.com). Solutions and buffers were prepared with deionized water and deoxygenated by purging with purified nitrogen gas. Tryptophan stock solutions were prepared freshly before each experiment. A phosphate buffer (PBS) of 0.1 M was employed as a supporting electrolyte, and the pH values were adjusted with NaOH and H_3PO_4.

2.2. Apparatus and methods

The thermogravimetric analysis (TGA) was measured by using HCT-3 analyzer under N_2 atmosphere and the heating rate was 10 °C min^{-1} from 40 to 850 °C. The surface morphology and structure of the samples were characterized via scanning electron microscopy (SEM, JEOL JSM-6480) and transmission electron microscope (TEM, FEI Tecnai G2 S-Twin, Philips). X-ray diffraction (XRD) analysis was conducted using Rigaku TTR III with Cu Ka (1.5142 Å) radiation. N_2 adsorption/desorption measurements were carried out on a Micromeritics ASAP 2020 analyzer at 77 K. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. All electrochemical measurements were performed on a CHI 900C electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). A typical three-electrode system was used, including the nanoporous carbon modified electrode as working electrode, a standard calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode.

2.3. Synthesis of nanoporous carbon

The nanoporous carbon was synthesized by a facile pyrolysis method, using phosphoric acid as the activating agent. The dandelion pappus collected from the outskirts of Harbin (China), was first washed with deionized water to remove impurities and dust. After drying, the pappus was then cut into pieces of 1–2 mm in size using scissors, and this fraction was used as precursor. A certain amount of precursor was added into the H_3PO_4 solution (85%) at the weight ratio of pappus: H_3PO_4 = 1:3. After soaking for 8 h, the impregnated pappus was dried at 50 °C for 24 h to ensure a complete evaporation of the moisture. Thereafter, the pretreated samples were subjected to heat treatment at 140 °C for 6 h in an oven. The resultant mixture was transferred into a tubular furnace and heated at 700 °C for 1 h under nitrogen atmosphere. Finally, the obtained nanoporous carbon was washed repeatedly with hot (100 °C) and cold deionized water to remove excess acid and then dried at 105 °C overnight under vacuum.

2.4. Preparation of the modified GCE

The black suspension of NPC was prepared by dispersing 2 mg of NPC in 2 mL dimethylformamide with the help of ultrasonication. Prior to surface modification, the GCE was polished with 0.3 and 0.05 μm alumina slurry and cleaned ultrasonically in water. 10 μL NPC suspension was casted onto the GCE surface and dried at room temperature to fabricate NPC-based modified electrode.

3. Results and discussion

3.1. Choice of materials

Fig. 1 shows the TGA and DTG curves of the dandelion pappus. It is easy to discover that the first step of weight loss from 40 to 140 °C is about 7.1%, which can be attributed to the release of moisture in the samples. The majority of the weight loss appears between 140 °C and 550 °C. In the next temperature range 140–343 °C, the decomposition of hemicellulose and cellulose is mainly responsible for the observed weight loss (45.5%) [24]. The third weight loss (24.82%) occurs at a range of 343–550 °C, which is assigned to lignin decomposition. Above