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Graphitic carbon nitride nanosheets modified multi-walled carbon nanotubes as 3D high efficient sensor for simultaneous determination of dopamine, uric acid and tryptophan

Cun Wang, Jun Li, Xueyan Luo, Junmin Hui, Xi Liu, Jun Tan, Xin Zhao *

Chongqing Collaborative Innovation Center for Functional Food, Chongqing Engineering Research Center of Functional Food, Chongqing Engineering Laboratory for Research and Development of Functional Food, Chongqing University of Education, Chongqing 400067, China

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) nanosheets, as graphene-like ultrathin semiconductor material, have strong covalent bonds between carbon and nitride atoms. The nitrogen atoms doping in the carbon architecture that greatly enhancing electrical properties and accelerating the electrontransfer rate, which can improve the electrical properties of g-C_3N_4 nanosheets. Herein, a novel electrochemical sensor was developed by immobilizing a three-dimensional (3D) hybrid nanocomposite which consisted of one-dimensional (1D) multi-walled carbon nanotubes (MWNTs) and two-dimensional (2D) g-C_3N_4 nanosheets on a glassy carbon electrode (g-C_3N_4/MWNTs/GCE). The g-C_3N_4/MWNTs/GCE exhibited excellent response toward the oxidation reactions of dopamine (DA), uric acid (UA) and tryptophan (Trp). Under the optimum conditions, the electrochemical sensor was used in the detection of DA, UA and Trp, and achieved wide ranges of 2.0–43.5 μM, 5.0–189.0 μM and 65.0–1815.0 μM with low detection limits (S/N = 3) of 5.0×10^{-8} M, 5.0×10^{-7} M and 1.0×10^{-6} M, respectively. In addition, the coexistence of ascorbic acid (AA) has no obvious interference toward the detection of DA, UA and Trp. Thus, the modified electrodes were successfully applied for the determination of DA, UA and Trp in urine and serum samples using the standard adding method with satisfactory results.

1. Introduction

Graphitic carbon nitride (g-C_3N_4), composing covalent bonding of carbon and nitrogen by π-conjugated, is the most stable allotrope of carbon nitride with high thermal and chemical stability. Owing to the outstanding catalytic properties and unique electron/optical properties, the g-C_3N_4 has attracted considerable attention in the fields of catalysis, degradation and sensor [1–5]. However, the poor electrical conductivity limited the application of g-C_3N_4 in electrochemical sensor [6,7]. To overcome this shortcoming, many efforts have been made to enhance the electrical conductivity of g-C_3N_4, such as, doping with metal nanopaticles or carbon material [8,9], copolymerizing with organic compounds [10], surface heterojunction designing with semiconductors [11] and coupling with graphene [12]. Meanwhile, owing to the advantages such as high electronic conductivity, good mechanical and chemical stability, and high specific surface areas, multi-walled carbon nanotubes (MWNTs) has attracted tremendous attention for their applications in a wide variety of areas [13–16]. Based on above, we attempted to explore the combination of g-C_3N_4 with well-conductive MWNTs to obtain a novel hybrid nanomaterial with exceptional properties for electrochemical catalysis.

Dopamine (DA), as a natural catecholamine formed by the decarboxylation of 3,4-dihydroxyphenylalanine, plays pivotal roles in the metabolism of renal, cardiovascular, central nervous and hormonal systems of human body [17,18]. Abnormal levels of DA may result in serious neurological disorders, such as Parkinson's disease, schizophrenia and Huntington's disease [19]. Uric acid (UA), as the end product of the metabolism of purine, is an important biomolecule existing in body fluids such as blood or urine. Several diseases such as Lesch–Nyhan Fanconi syndrome, renal disease and hyperuricemia are related with the abnormal concentrations of UA [19,20]. As an essential amino acid, tryptophan (Trp) is a precursor of the neurotransmitter serotonin, which is important in nitrogen balance and the maintenance of muscle mass and body weight in humans and herbivores [21,22,23]. In sum, DA, UA and Trp are very important small biomolecules in metabolism of human body, which are usually coexisting in real biological matrixes. Therefore, developing an effective, accurate and sensitive approach to detect DA, UA and Trp is highly imperative. Due to the high sensitivity, rapid responsivity, simple operation and low cost, electrochemical sensor has been widely used in the detection of DA, UA and Trp [24]. However, owing to the overlap of the oxidation peaks of DA, UA and Trp in voltammetric response on the bare electrode, it is difficult to realize

* Corresponding author.
E-mail address: zhaoxin@cque.edu.cn (X. Zhao).

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their simultaneous detection [23]. To overcome this problem, various modified electrodes have been developed to solve the above problem, such as polymers [25], metal nanoparticles [26], metal nanoparticle/polymer composites [23,27], carbon based composites [17,18].

Inspired by above studies and our previous researches [28,29], we develop a sensitive voltammetric protocol for the simultaneous determination of DA, UA and Trp by using the three-dimensional (3D) g-C_3N_4/MWNTs hybrid nanomaterial modified glass carbon electrode (g-C_3N_4/MWNTs/GCE). The g-C_3N_4 is bridged to MWNTs via π–π stacking interaction to form porous and loose structures. Based on the above advantages, the g-C_3N_4/MWNTs/GCE exhibits high sensitivity for the simultaneous detection of DA, UA and Trp with no electrochemical interference under the existence of AA. More importantly, the sensor has been used for the determination of these compounds in human serum and urine samples successfully.

2. Materials and methods

2.1. Chemicals

Multiwalled carbon nanotubes and chitosan were purchased from Sigma Chemical Co. (St. Louis, Mo, USA). Melamine (2,4,6-triamino-1,3,5-trazine, 99%) was obtained from Aladdin Ltd. (Shanghai, China). Uric acid (UA), ascorbic acid (AA), dopamine (DA), tryptophan (Trp), Na_2HPO_4, KH_2PO_4 and KCl were purchased from Chemical Reagent Co. (Chongqing, China). Phosphate buffer solutions (PBS) (0.1 M) at various pH were prepared using 0.1 M Na_2HPO_4 and 0.1 M KH_2PO_4. The supporting electrolyte was 0.1 M KCl. Double-distilled water was used throughout the experiments. Chitosan solution was prepared by dissolving 0.5 g chitosan solid in 100 mL 0.10 M acetic acid.

2.2. Apparatus

Cyclic voltammetric measurements and differential pulse voltammetry measurements experiments were performed with a CHI660E electrochemical work station (Shanghai Chenhua Instrument Co., China). A conventional three-electrode system was used with a modified glassy carbon electrode (GCE) electrode as working electrode, a saturated calomel reference electrode (SCE), and a platinum wire auxiliary electrode. Scanning electron micrographs were obtained using a scanning electron microscope (SEM, Hitachi, Japan). All measurements were carried out at room temperature.

2.3. Synthesis of g-C_3N_4 nanosheets

The g-C_3N_4 nanosheets were synthesized by thermal polycondensation of melamine according to the previous reported method in the literature with a little modification [30,31,32]. In detail, first, 20.0 g melamine was added into an alumina crucible and heated at 600 °C for 2 h in a muffle furnace with a heating rate of 5 °C min^{-1}. The reaction products were collected and ground into yellow bulk g-C_3N_4 powder after cooling to room temperature. Then, 0.5 g g-C_3N_4 powder was ultrasonicated in 500 mL water for 10 h. After that, the obtained suspension was centrifuged at 5000 rpm to remove the remaining residual unexfoliated bulk g-C_3N_4. Finally, the liquid supernatant was dried in air to obtain the g-C_3N_4 nanosheets.

2.4. Electrode preparation and modification

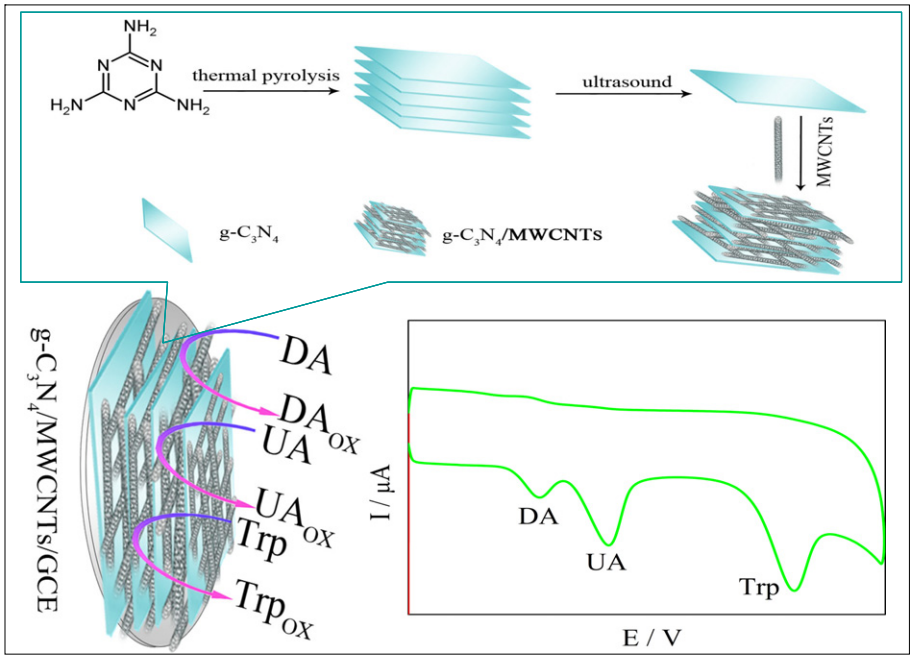
Before modification, the bare glassy carbon electrode (GCE, diameter 4.0 mm) was successively polished using 0.3 and 0.05 μm alumina slurry until a mirror-like surface was acquired, then sonicated in ethanol and double-distilled water successively and dried at room temperature.

The g-C_3N_4/MWNTs nanocomposites were prepared by dispersing 1.0 mg resulting g-C_3N_4 and 1 mg MWNTs in 5 mL chitosan (CS) solution, and then the mixture was treated for 1 h with ultrasonication for uniform dispersion. The g-C_3N_4/MWNTs/GCE was prepared by casting 20 μL of the above-mentioned suspension on the surface of the GCE. The modified electrode was dried at room temperature and rinsed with distilled water prior to use. For comparison, g-C_3N_4/GCE and MWNTs/GCE were also prepared under the same conditions.

3. Results and discussion

3.1. The fabrication of g-C_3N_4/MWNTs nanocomposites modified electrode

The illustration of the fabrication of g-C_3N_4/MWNTs nanocomposites modified electrode was shown in Scheme 1. First, the g-C_3N_4 and g-



Scheme 1. Schematic diagram of the fabrication procedure g-C_3N_4 and g-C_3N_4/MWNTs, and the g-C_3N_4/MWNTs/GCE was used direct determination of DA, UA and Trp.