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Regular Article

Green synthesis of a novel flower-like cerium vanadate microstructure for electrochemical detection of tryptophan in food and biological samples

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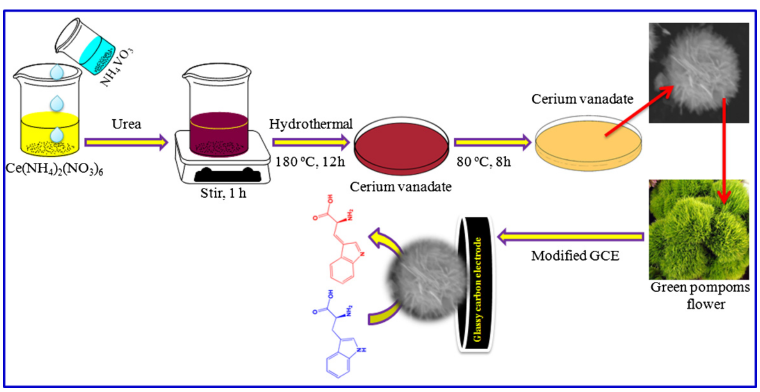
GRAPHICAL ABSTRACT



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ABSTRACT

In this present investigation, we introduced a novel electrochemical sensor for the detection of tryptophan (TRP) based on green pompoms flower-like cerium vanadate ($CeVO_4$). The flower-like $CeVO_4$ microstructure was prepared by the simple hydrothermal treatment with the assistance of urea for the first time. The as-prepared flower-like $CeVO_4$ microstructure was characterized by various analytical and spectroscopic techniques such as X-ray diffraction, Raman spectroscopy fourier transform infrared spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy studies. The electrochemical properties are evaluated by the cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As an electrochemical sensor, the green pompoms flower-like $CeVO_4$ modified glassy carbon electrode (GCE) displayed an excellent electrocatalytic activity for the detection of TRP. The obtained electrochemical results revealed that the oxidation of TRP, exhibited a lower potential and higher anodic peak current when compared to unmodified GCE. These results were suggested that the flower-like $CeVO_4$/GCE have a good electrocatalytic activity towards the TRP oxidation. The flower-like $CeVO_4$ sensor exhibited the wide linear concentration range and low detection limit of 0.1–94 μM and 0.024 μM respectively. Finally, the proposed sensor was successfully applied to the determination of TRP in real sample analysis such as food and biological samples with satisfied recoveries.

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1. Introduction

Nowadays, most of the researchers have been focused on the determination of molecular recognition of various amino compounds such as amino acids, proteins and biological amines due to their biological importance. Among them, amino acids are playing an essential role in the human neuroregulation, metabolism, organ function process, etc. [1]. Tryptophan (2-amino-3-(1H-indol-3-yl)-propionic acid, TRP) is one of the important amino acid for the growth and metabolism functions of human as well as animals. In contrary, the improper metabolism of TRP would generate a waste products in the brain which causes delusions, depressions, hallucinations, Alzheimer's and Parkinson's diseases [2,3]. Regrettably, our human body cannot generate TRP directly and thus it is gained from milk, bananas, dried dates, oats, chocolates, egg, dietary and pharmaceutical products. The World Health Organization (WHO) listed as the daily minimum requirement of TRP is 4 mg per kg of body weight [4]. However, the higher intake of TRP would diminish the pathological plaques in Alzheimer disease and also induces loss of appetite, dizziness, drowsiness and nausea [5,6]. In addition, the concentrations of TRP in human blood plasma is associated with the hepatic diseases as well as it can be identified as a precursor for the neurotransmitter serotonin, niacin and neurohormone melatonin [7]. Therefore, the simple, effective and accurate detection of TRP in the biological, food products and pharmaceutical samples is an important concern to prevent the human health. Until now, various efforts have been developed for the detection of TRP including high pressure liquid chromatography, flow injection, chemiluminescence, chromatography-spectrophoto metry, colorimetry and electroanalysis methods [8]. Among all, the electrochemical techniques are more adoptable due to its simplicity, low-cost, fast response, practicality, high sensitivity and good selectivity [9–11].

In recent years, metal vanadates have been paid tremendous interest owing to their environment benignity, excellent redox and electrochemical properties. Hence, they have been widely used as a various potential applications such as lithium ion batteries, luminescent materials, optical materials, semiconductors, ceramics, magnetic materials, photocatalysis and catalysis [12]. Among the vanadates, rare earth orthovanadates (RE-VO_4, RE = Ce, Pr, La) have been attained enormous interest due to their good electrical properties, high surface area, thermal stability, optical and magnetic properties [13]. In particular, cerium vanadate ($CeVO_4$) is an important member of rare earth vanadates which has been extensively used as numerous applications such as catalysis [14], counter electrodes [15], gas sensors [16], photocatalytic and super hydrophobic material [17], solar cells and supercapacitors [18], lithium-ion batteries [19] due to its excellent redox behavior, thermal stability, electrical and optical properties and 4f electronic nature. Furthermore, to improve their physicochemical properties various morphologies have been developed including hollow nanospheres [20], nanorods [16], nanoplates [17], nanobelts [18] and nanoparticles [19]. However, a new morphology is always an ultimate aim to extend/enhance the performances of $CeVO_4$ and it open up a new begin. Since, the detection of TRP using several electrochemical sensors are limited and showed poor response. Moreover, the trace level detection of TRP in the biological samples has not been explored. Hence, the sensitive and rapid detection of TRP attains more interest in biomedical, industrial and environmental analysis. Up to now, to the best of our knowledge, there is no reports were available for green pompoms flower-like $CeVO_4$ microstructure and its applications for the selective electrochemical detection of TRP.

Herein, we developed a novel electrochemical sensor for the detection of TRP based on a flower-like $CeVO_4$ modified GCE. The flower-like $CeVO_4$ synthesized via simple hydrothermal route with assistance of urea and it was characterized and explained in detail. The electrochemical studies were investigated by CV and DPV. Furthermore, as-prepared $CeVO_4$ was fabricated on the glassy carbon electrode (GCE) by a simple drop casting method. Interestingly, the obtained electrochemical performance and voltammetric determination of TRP at the flower-like $CeVO_4$ modified GCE were studied in detail. The results revealed that the $CeVO_4$/GCE displayed good electrocatalytic activity for the oxidation of TRP.

2. Experimental section

2.1. Materials

Ammonium ceric nitrate ($Ce(NH_4)_2(NO_3)_6$), ammonium meta vanadate (NH_4VO_3), urea, tryptophan and all other chemical were purchased from Sigma-Aldrich and Merck companies, Taiwan & India and used without further purification. All the reagents and chemicals were of analytical grade and used as received. The required electrolyte used for the electrochemical studies (0.05 M phosphate buffer solution) was prepared by mixing of disodium phosphate (Na_2HPO_4) and monosodium phosphate (NaH_2PO_4). The electrolyte was adjusted by sulfuric acid and sodium hydroxide (for different pH studies). For the real sample analysis, the milk samples were purchased from the local market in Taipei, Taiwan.

2.2. Synthesis of green pompoms flower-like $CeVO_4$

In a typical procedure, 0.2 M $Ce(NH_4)_2(NO_3)_6$ and 0.1 M NH_4VO_3 were dissolved in 70 mL of de-ionized water. Then, 10 mL of 0.1 M urea was added into the above mixture and it was allowed to stir for 1 h. Subsequently, the mixture was transferred into 100 mL Teflon-lined sealed stainless steel autoclave and kept 180 °C for 12 h. After that, the autoclave was naturally cooled and the precipitate was collected, washed with water & alcohol, and dried at 80 °C for 8 h. The overall synthesis route for the preparation of green pompoms flower-like $CeVO_4$ and its electrochemical applications are shown in Scheme 1.

2.3. Fabrication of green pompoms flower-like $CeVO_4$ modified GCE

As-prepared $CeVO_4$ (3 mg/mL) was re-dispersed in de-ionized water. Before the modification of GCE, it was cleaned with 0.05 μm alumina slurry and thoroughly washed with copious amount of water. After that, the polished GCE surface was dried at room temperature. About 8 μl (optimized concentration) of the $CeVO_4$ suspension was drop casted on the GCE surface and it was allowed to dry at room temperature. Then that obtained $CeVO_4$ modified GCE surface was gently rinsed with water to remove the loosely attached molecule. The obtained $CeVO_4$ modified GCE was employed for further electrochemical measurements.

2.4. Characterization

The X-ray diffraction patterns of the material was recorded in a XRD, XPERT-PRO spectrometer (PANalytical B.V., The Netherlands) with CuKα radiation (λ = 1.5406 Å). Raman spectroscopy was analyzed using an NT-MDT, NTEGRA SPECTRA spectrometer. Fourier transform-infrared spectroscopy (FT-IR) studies were recorded by using FT/IR-6600 spectrophotometer. Scanning electron microscope (SEM) and Energy dispersive X-ray spectral studies were observed by using Hitachi S-3000 H scanning electron microscope (SEM Tech Solutions, USA) and HORIBA EMAX X-ACT, respectively. Cyclic voltammetry and Differential pulse voltammetry