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Pt-PEDOT/rGO nanocomposites: One-pot preparation and superior electrochemical sensing performance for caffeic acid in tea

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A R T I C L E I N F O

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A B S T R A C T

In this paper, Pt-PEDOT/reduced graphene oxide (Pt-PEDOT/rGO) nanocomposites were facilely prepared by a simple and cost-effective one-pot method. The obtained nanocomposites were characterized and confirmed by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectra. As expected, the Pt-PEDOT/rGO nanocomposites modified glassy carbon electrode (Pt-PEDOT/rGO/GCE) exhibited higher charge transfer efficiency and electrocatalytic activity to the oxidation of caffeic acid (CA) in comparison with the bare GCE, rGO and Pt-PEDOT modified electrodes (rGO/GCE and Pt-PEDOT/GCE). Furthermore, the Pt-PEDOT/rGO/GCE showed a wide linear range of 5.0×10^{-9} to 5.0×10^{-5} M with a low detection limit of 2.0×10^{-9} M (S/N = 3) for the determination of CA. More experiments indicated that the Pt-PEDOT/rGO/GCE performed superior reproducibility, selectivity and long-term stability. Finally, the modified electrode was also applied to detect CA in green tea and black tea samples with promising recovery and application prospect.

1. Introduction

Phenolic compounds, as secondary metabolites in plants, are widely found in fruits and vegetables such as apples, berries, onions, tomatoes as well as in beverages as teas, wines, and fruit juice [1,2]. Caffeic acid (CA) is one of the most important phenolic acids because of its several pharmacological actions, such as anti-inflammatory, antimicrobial, antioxidant and immunomodulatory [3–6]. Especially, some studies showed that CA can stop HIV from replicating as an inhibitor of HIV-1 integrase [7]. There is no doubt that the quantitative determination of CA has important meanings to people's healthy diet.

In recent years, all kinds of analytical methods have been developed to detect CA, such as spectrophotometry [8], high performance liquid chromatography [9] and capillary electrophoresis [10]. However, these methods usually need expensive instruments and professional technicians. In other words, they are high-cost and time consuming during the determination. Electrochemical techniques, especially cyclic voltammetry (CV) and differential pulse voltammetry (DPV) has attracted much interests in the detection of CA, because they are easy to operate, fast, cost-effective, highly sensitive and selective [11,12].

For electrochemical methods, the choice of a suitable electrode material is crucial. Thus, various electrode materials have been prepared and reported for the detection of CA [13–17]. Graphene-based material, like rGO, has been widely applied in the field of electrochemical detection of CA owing to its large specific surface area, high mechanical properties, thermal conductivity and superior electrochemical performance [2,19–22]. A.T. Ezhil Vilian et al. prepared a chemically reduced graphene oxide modified glassy carbon electrode (CRGO/GCE) for electrochemical determination of CA with a wide linear range of 1×10^{-8} to 8×10^{-4} M and a detection limit of 2×10^{-9} M [23]. Just like graphene, noble metal nanoparticles, such as Pt, Pd, Au and Ag, have also attracted extensive attention in electrochemical sensor field, because of their outstanding electrocatalytic activities and conductivities [24,25]. However, agglomeration and aggregation easily occur during the deposition of these metal particles chemically or electrochemically, which will severely affect their specific surface area as well as electrocatalytic activity. Herein, many other functional materials (such as nano-carbon materials and conducting polymers) have been introduced and composited with the noble metal particles to improve their dispersibility and enhance their electrochemical active surface [26–28]. Poly(3,4-ethylene-dioxythiophene) (PEDOT), as one of the "star conducting polymer", has always been the research hotspot in sensor, supercapacitor, battery and so on [29–31], because of its good biocompatibility and high environmental stability, electrical conductivity and permeability in oxide films [32]. Especially, PEDOT has been composited with metal nanoparticles by some

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researchers for the electrochemical detection [33,34]. In our previous work, Au-PEDOT and Pd-PEDOT nanocomposites were prepared by this method without adding other oxidants and stabilizers, then Au-PEDOT/rGO and Au-Pd/PEDOT/rGO nanocomposites were synthesized successfully by one-pot method for the determination of CA. They all had a high electrocatalytic activity to CA oxidation, the Au-PEDOT/rGO/GCE exhibited a linear range of 0.01–46 μM with a detection limit of 0.004 μM, and the Au-Pd/PEDOT/rGO/GCE had a wider linear range of 0.001–55 μM with a lower detection limit of 0.00037 μM [11,12]. As far as we know, there is only one report on the preparation of Pt-PEDOT/rGO nanocomposite for methanol oxidation by conventional chemical method [35]. But in our research, we simply synthesized Pt-PEDOT under heating, then we prepared the Pt-PEDOT/rGO nanocomposite by one-pot method for the first time, which is a facile, “green” and high efficiency method.

In this study, we prepared Pt-PEDOT/rGO nanocomposite for the CA detection by a new method. Its performance for the detection of CA was investigated by cyclic voltammetry and differential pulse voltammetry. In addition, the reproducibility, selectivity and long-term stability of the Pt-PEDOT/rGO/GCE were studied. Its excellent electrocatalytic performance is mainly due to the high catalytic properties of Pt nanoparticles and the super electrical conductivity of PEDOT and rGO.

2. Experimental

2.1. Chemical reagents

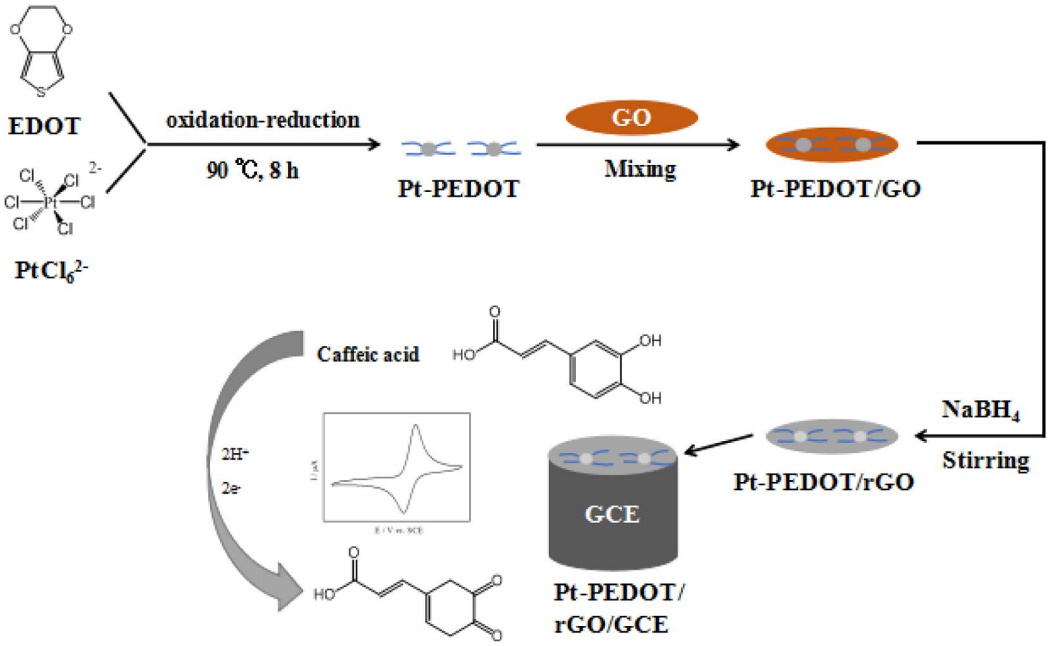
3,4-Ethylenedioxythiophene (EDOT) was purchased from Aldrich Chem Co. (USA). Graphene oxide (GO) was bought from Nanjing Xianfeng nano Co. Caffeic acid was obtained from Sinopharm Chemical Reagent Co. Ltd. Chloroplatinic acid and other reagents were purchased from Aladdin Chemistry Co., Ltd. The teas were bought from supermarket. All these reagents were analytical grade and used without further purification. The Britton-Robinson (BR) buffer solutions were prepared from a mixture of 0.04 M boric acid, glacial acetic acid and phosphoric acid aqueous, and the pH value of the buffer solutions was adjusted with 0.2 M sodium hydroxide solution. Deionized water was used for the preparation of solutions in the experiment.

2.2. Instrumentation

The morphology and structure of the composite were characterized with a scanning electron microscopy (SEM, S-4800, Japan) and transmission electron microscopy (TEM, Tecnai G2 F20). X-ray diffraction (XRD) spectra were analyzed by a Brooke D8 Advance X-ray diffraction instrument. Raman spectra were obtained from a LabRAM HR 800 Raman analyzer (Longjumeau, France). X-ray photoelectron spectra (XPS) were performed by a Thermo Scientific ESCALAB 250Xi spectrometer. All electrochemical experiments were performed on a CHI 660D electrochemical workstation (ChenHua Co., Shanghai, China) with a conventional electrochemical three-electrode system consisting of a Pt wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode and a modified GCE as working electrode, respectively.

2.3. Synthesis of Pt-PEDOT/rGO nanocomposite

First, 5 mL of EDOT ethanol solution (13.5 mM) was slowly poured into the 40 mL chloroplatinic acid solution under stirring, then the obtained mixture was heated to 90 °C, and reacted for 8 h at this temperature. In this process, EDOT was oxidized to PEDOT, and the $PtCl_6^{2-}$ was reduced to Pt. When the mixture was cooled to room temperature, added 3 mL of GO dispersion (0.5 $mg\,mL^{-1}$), Pt-PEDOT/GO mixture solution was obtained, and the solution was sonicated for 2 h. Subsequently, 6.6 mL of $NaBH_4$ solution (0.16 M) was added into the mixture drop by drop, the reaction was lasted for 6 h with stirring. Finally, the obtained Pt-PEDOT/rGO mixture solution was centrifuged and washed three times with ethanol and water in turn, then dispersed to 40 mL deionized water (Scheme 1). In addition, in the preparation of Pt-PEDOT/rGO nanocomposite, some reaction conditions were optimized, including the mole ratio, reaction time of $PtCl_6^{2-}$ and EDOT, and the content of graphene oxide. As a result, when the mole ratio of $PtCl_6^{2-}$/EDOT was 1/4, the reaction time of $PtCl_6^{2-}$ and EDOT was 8 h, and adding 2 mg GO per 20 mL obtained Pt-PEDOT solution, the obtained Pt-PEDOT/rGO nanocomposite had the best effect on the electrocatalytic oxidation of caffeic acid. Therefore, we had prepared the Pt-PEDOT/rGO nanocomposite under these conditions for subsequent study. The Pt-PEDOT solution and rGO solution were obtained in the same conditions for comparision.



Scheme 1. Schematic illustration for the preparation of Pt-PEDOT/rGO/GCE.