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Enhanced TA determination on 3D flower-like ZnO-Pt nanocomposites under ultraviolet light illumination

Shumin Li[a], Ke Zhang[a], Jin Wang[a], Bo Yan[a], Caiqin Wang[b,*], Zhiping Xiong[a], Hui Xu[a], Yukou Du[a,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] Chemistry Department, University of Toronto, Toronto, M5S3H4, Canada

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ABSTRACT

Flower-like ZnO-Pt materials with three-dimensional architectures were synthesized by one-pot method, and a novel tannic acid (TA) analytical method based on flower-like ZnO-Pt modified glassy carbon electrode (ZnO-Pt/GCE) was also developed. Due to the introduction of metal Pt on ZnO, the as-prepared electrode exhibited good conductivity and gave rise to a significant increase in the photocurrent density under UV light illumination, confirming an enhanced charge transfer speed and a well combination between exited electron-hole pairs of ZnO. For the analysis of TA, differential pulse voltammetry (DPV) was applied to evaluate the photoelectrochemical performance on ZnO-Pt/GCE, and a wide linear range of 0.04–72.34 μM with a low detection limit of 0.02 μM (at S/N = 3) was obtained ultimately. The oxidation mechanism of tannic acid in different routes was also proposed and discussed. Moreover, the prepared electrode displayed high stability and selectivity toward the determination of tannic acid. These excellent results presented here make the ultraviolet assisted electrochemical determination a promising method in sensing.

1. Introduction

Ultraviolet (UV) light technique has attracted considerable interest owing to its diverse application in many areas, such as UV photocatalytic oxidation, chemical and biochemical sensing, environmental monitoring, astronomical research and geological survey [1–3]. As one of important semi-conductor nano-photocatalysts, ZnO, a direct band gap (~3.37 eV) semiconductor with a large excitation energy of 60 meV, is a promising candidate because of its good electrical catalytic and optical properties [4,5]. Under UV light irradiations, the electrons on the valence band are excited to the conduction band, but the recombination of the active electrons and holes limited the photocatalytic efficiency of ZnO [6]. Thus, the design of metal/ZnO nanocomposite structure has become an effective strategy to regard the recombination between exited electrons and holes. Especially for platinum (Pt), which is one of the best choices among noble metals due to its large specific surface areas and a large work function of 5.93 eV [2]. The Scotty barrier is formed after a hybrid between metal Pt and ZnO, and excited electrons would be more likely to leap from the valance band and transfer to metal Pt. When irradiated with UV light, this rectification effect decreases free electrons of ZnO that may participate in the recombination effectively and leads to a high photocatalytic performance [7–9]. Several excellent reviews have described the catalytic properties of ZnO-Pt in photo-electrochemical application. For example, Yuan et al. has reported on the photocatalytic behaviors of ZnO-Pt nanoflowers, and an improved catalytic efficiency is obtained compared with bare ZnO [6]. An interesting approach for glucose determination by PtNPs/ZnO nanowires under UV illumination is described by Hsu et al., this photo-electrochemical method has a superior sensitivity than previous studies [7].

Tannic acid (TA), a mixed compound gallotannin consists of a central carbohydrate and 10 galloyl groups, and the chemical structure of TA is shown in Scheme 1. It is a water hydrolyzed polyphenolic compound, which is abundant in different kinds of fruits and vegetables [10]. What's more, TA is widely applied in both research and industry filed, such as its application for an addictive in medical products for treating diarrhea and burns, clarifying agent and flavoring agent in food industry, as well as its great importance for re-tanning in combination with Cr (III) salt to prevent leather putrefaction [11–13]. In view of its widespread uses, an effective and fast detection method for TA is urgently sought. Especially TA as an organic chemical in tanning industry, is considered as a pol-

* Corresponding authors.
E-mail addresses: miss.xiaocai@163.com (C. Wang), duyk@suda.edu.cn (Y. Du).

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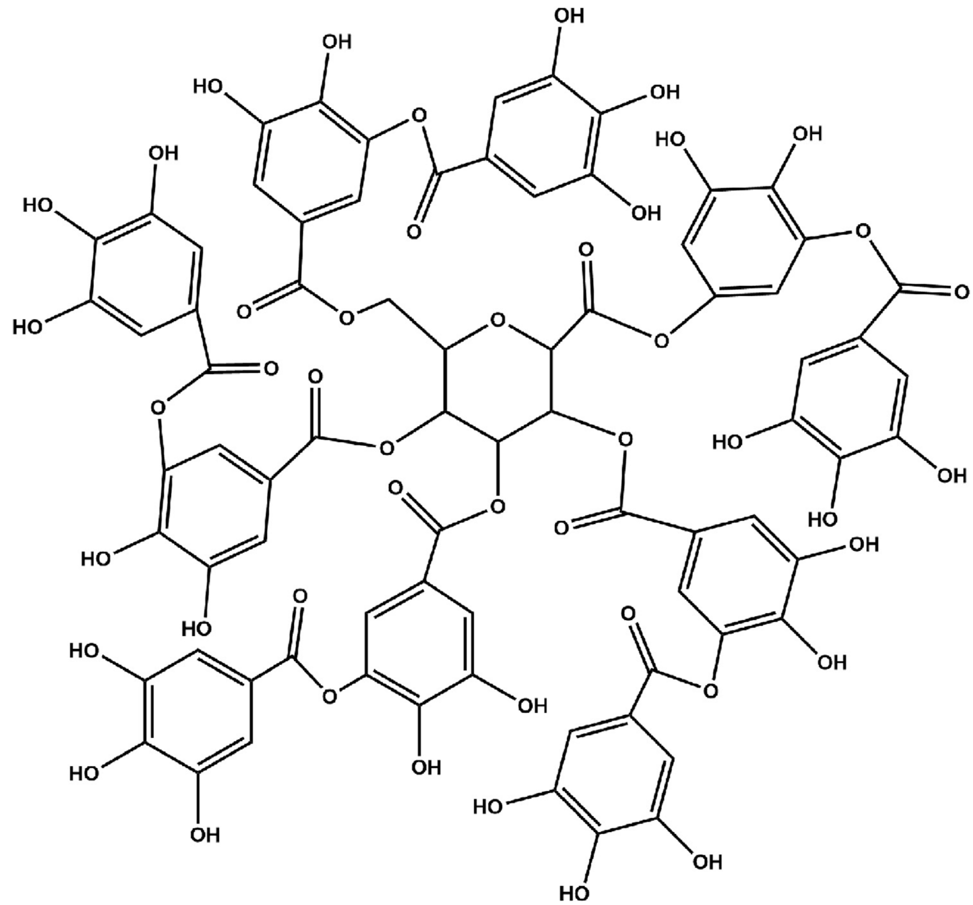

Scheme 1. Chemical structure of tannic acid.

lutant that may contaminate the aquatic ecosystem and has been discovered to be toxic to aquatic microorganisms [14]. Therefore, the analysis of TA is of importance not only in food and pharmacological industry to ensure human health but also in environmental fields to protect nature environment. Much work so far has focused on TA determination, including electrochemical methods [15,16], chromatography [17], luminescence [18] and spectrophotometry [19]. However, some detection methods are time-consuming and expensive, and the detection range is always narrow [15,17]. Hence, it is still a challenge to develop fast, sensitive and effective analytical methods for tannic acid.

Herein, we report a hydrolysis method for the successful synthesis of 3D flower-like ZnO-Pt nanostructure, and a novel photo-electrochemical approach for the determination of tannic acid. The performance of ZnO-Pt/GCE has been evaluated by differential pulse voltammetry method under UV light irradiations. Taking advantage of good photoenergy conversion efficiency of ZnO and high catalytic reactivity of platinum nanoparticles, ZnO-Pt/GCE exhibits a low detection limit and a wide linear range toward TA detection. Also, the prepared electrode displays a good potential both in stability and selectivity in TA sensing. Therefore, we expect that the promising material of 3D flower-like ZnO-Pt has a further use in photocatalysis and practical application.

2. Experimental

2.1. Reagents and apparatus

Double distilled water was used throughout the study. Chloroplatinic acid (H_2PtCl_6) was purchased from Shanghai Shiyi Chemicals Regent Co., Ltd, China. Zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$), ammonia ($NH_3\cdot H_2O$), hydrazine hydrate ($N_2H_4\cdot H_2O$, 80%), potassium ferrocyanide ($K_4Fe(CN)_6$), potassium ferricyanide ($K_3Fe(CN)_6$), sodium dihydrogen phosphate dehydrate ($NaH_2PO_4\cdot 2H_2O$), sodium phosphate dibasic anhydrous (Na_2HPO_4), phosphate acid (H_3PO_4), potassium chloride (KCl), ammonium bromide (NH_4Br), sodium hydroxide (NaOH), ascorbic acid (AA), glucose ($C_2H_{12}O_6\cdot H_2O$) and ethanol (C_2H_5OH) were purchased from Sinopharm Chemicals Reagent Co., Ltd, China. All reagents were analytical grade and were used without any further purification. Freshly prepared 0.1 M phosphate buffer solution was also used in experimental process.

The morphology and structure of the nanocomposites were studied by scanning electron microscopy (SEM) and energy-dispersive X-ray analyzer (EDX) with the S-4700 system (Hitachi High Technologies Corporation, Japan). X-ray diffraction (XRD) analysis was carried out on a PANalytical X'Pert PRO MRD X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å) operated at 40 kV and 30 mA. X-Ray photoelectron spectroscopy (XPS) was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The electrochemical experiments were carried out on a CHI 660D electrochemical station (Shanghai Chenhua Instrumental Co., Ltd, China) with a conventional three-electrode system. The glassy carbon electrode (GCE) with a surface area of 0.07 cm^2 was made with a working electrode.

2.2. Preparation of flower-like ZnO-Pt nanostructures

In a typical synthesis of ZnO-Pt nanostructures, $Zn(NO_3)_2\cdot 6H_2O$ (0.1821 g) and H_2PtCl_6 (1 mL, 22.43 mM) were dissolved in 60 mL