



Research paper

Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) on terbium hexacyanoferrate for sensitive determination of tartrazine



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ABSTRACT

We report the facile electrochemical method for the preparation of poly(3,4-ethylenedioxythiophene) (PEDOT)@Terbium hexacyanoferrate (TbHCF) composite on glassy carbon electrode (GCE). The as prepared PEDOT@TbHCF composite was characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy and Electrochemical Impedance Spectroscopy (EIS). Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) were performed for analyzing the electrochemical sensing of tartrazine (Tz). The PEDOT@TbHCF/GCE exhibits wide linear range, high sensitivity, and low limit of detection of about 0.1–206 μM , $1.24 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ and 0.032 μM , respectively. The real sample analysis reveals the practical applicability of PEDOT@TbHCF/GCE for sensing of Tz in food samples.

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1. Introduction

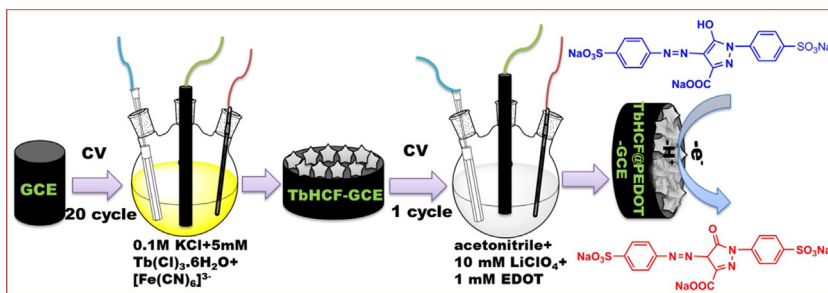
Tartrazine (Tz) ($\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$) is a kind of bright yellow azo food coloring dye and this synthetic food dye is the derivative of coal-tar and nitrous. It is widely used in many foods, medications, personal care and cosmetics products such as ice creams, cotton candy, cake, soft drinks, jelly, chewing gums, noodles, liquid bar soaps, mouthwashes, perfume, nail polish, and shampoo *etc* [1]. Hence, it is considered as an important coloring dye and also many countries listed the Tz as a permitted food dye. Though it was permitted worldwide, the usage must be limited due to the serious side effects such as asthma, thyroid cancer, permanent DNA damage, and itching *etc*. [2]. Therefore, the effective techniques are evolving for the determination of Tz to avoid serious allergies. Abundant methods have been followed for the detection of Tz including, HPLC [3], stopped-flow analysis [4], spectrophotometry method [5] and fluorescence method [6]. But these above-mentioned techniques have many disadvantages such as complex sample preparation procedure, sample pretreatment involving separation, extraction and adsorption with long analysis time and high cost [7,8]. Hence, the electrochemical technique is

more significant and substantial attractive technique owing to its inexpensive diagnostic tools, easy sample preparation, high sensitivity, long-term stability, reproducibility and high selectivity in sensing of analytes [9,10]. Moreover, Tz has been electrochemically determined by using different types of modified electrodes based on carbon nanomaterials [11–16], carbon nanomaterials composites with metal oxides [17], polymers [18,19] and metal nanoparticles [20–22].

In recent years, new and innovative materials such as carbon nanomaterials, metal oxides/hydroxides, and metal nanoparticles have been found with exclusive properties for various applications. In this list, metal hexacyanoferrate (MHCF) has been found as a new kind of inorganic poly-nuclear compound with zeolite structure. These kinds of materials have been used for several applications including supercapacitors [23], batteries [24], electrocatalysis [25], photocatalytic devices [26] and sensor [27]. Especially, MHCF has been focused on sensor applications owing to its good reversible redox process with low dissolution ability in solution and high stable film forming on the deposited substrate [28]. Both chemical and electrochemical synthesis has been widely used for the preparation of MHCF. The chemical synthesis is considered as a time-consuming process due to following on number of steps during the synthesis [29]. Alternatively, the electrochemical deposition of MHCF is considered to be an excellent way to prepare the stable film with unique morphology and crystallinity. For example, the variety of metal hexacyanoferrates has been prepared using electrochemical deposition with different morphology such as dysprosium hexacyanoferrate [30], samarium hexacyanoferrate [31],

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Scheme 1. Schematic illustration of the preparation of PEDOT@TbHCF/GCE and the mechanism for the electrochemical oxidation of Tz.

cerium hexacyanoferrate [32], yttrium (III) hexacyanoferrate [33], praseodymium hexacyanoferrate [34].

Suling Yang et al prepared the chemically synthesized flower-globular Terbium Hexacyanoferrate (TbHCF)/graphene for nanomolar detection of rutin [35] and Qinglin Sheng et al. Prepared sol-gel derived TbHCF for the oxidation of ascorbic acid [36]. Further to extend the application of electrodeposition and minimize the time consumption, the electrochemical deposition was followed for the first time to prepare the TbHCF. Here, TbHCF was electrochemically deposited on glassy carbon electrode (GCE). Afterward, 3,4-ethylenedioxythiophene was electropolymerized on pre-deposited TbHCF modified GCE to improve its stability. In reported works, the metal nanoparticle incorporated poly(3,4-ethylenedioxythiophene) (PEDOT) was used to form a stable and homogenous film [37] and utilized as a sensing matrix [38]. In addition, the PEDOT is performing as a charge transfer path with excellent electrochemical stability [39] and an electrochemically deposited PEDOT exhibits a higher stability in phosphate buffer than compared with other polymers [40]. Hence, PEDOT is suggested as a suitable polymer for sensor application and especially for food analysis [41]. In general, PEDOT is prepared using both chemical and electrochemical polymerization techniques. Among these two polymerizations, electrochemical polymerization has favorable advantages such as thin and rough surface polymer film can deposit on a small surface area with a high magnitude of geometrical conformity. Especially, the thickness can be controlled by adjusting the number of deposition cycles [42]. Eventually, an electrochemically deposited TbHCF@PEDOT matrix may exhibits the substantial electrocatalytic properties towards the determination of Tz as shown in Scheme 1.

2. Experimental section

2.1. Materials

Tartrazine, Terbium (III) chloride hexahydrate, 3,4-Ethylenedioxythiophene (97% of purity) and potassium chloride were purchased from Sigma-Aldrich. $K_3Fe(CN)_6$, Na_2HPO_4 , NaH_2PO_4 and $LiClO_4$ were purchased from Wako pure chemical industries. The supporting electrolyte 0.05 M phosphate buffer solution (PBS) (pH 5) electrolyte solution was prepared by mixing of 0.05 M Na_2HPO_4 and NaH_2PO_4 and the pH of the electrolytes solution was adjusted by $NaOH/H_2SO_4$. All the solutions were prepared using doubly distilled water (DD) and all chemicals are analytical grade and used without any further purifications.

2.2. Apparatus

Scanning Electron Microscopy (SEM) was performed by using Hitachi S-3000H electron microscope. Energy dispersive X-ray (EDX) spectrum was recorded using HORIBA EMAX X-ACT that was attached to Hitachi S-3000H scanning electron microscope.

XRD characterization was carried out using XPERT-3 diffractometer with $Cu K\alpha$ radiation ($K = 1.54 \text{ \AA}$). ITO plate was used during the XRD studies. Fourier Transform Infrared Spectroscopy (FTIR) measurement was recorded using JASCO FT/IR-6600. Raman spectroscopy was a recorded using WITech CRM200 confocal microscopy Raman system with a 488 nm laser. Electrochemical impedance spectroscopy (EIS) was performed using IM6ex ZAHNER impedance measurement unit, where Frequency range: 100 mHz to 100 KHz. The Cyclic Voltammetry (CV) was performed using CHI611A electrochemical analyzer. Differential pulse voltammetry (DPV) studies were performed using CHI900 electrochemical analyzer, while the potential window fixed from 0 to 1.1 V. The conventional three-electrode system was used in these following all electrochemical studies where glassy carbon electrode (GCE) was used as a working electrode, a saturated Ag/AgCl electrode used as a reference electrode and a platinum electrode used as the auxiliary electrode. All measurements were carried out at room temperature.

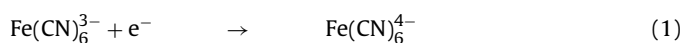
2.3. Preparation of TbHCF@PEDOT modified glassy carbon electrode (GCE)

The cyclic voltammetry technique was used for the electrodeposition of TbHCF on GCE. In beginning, GCE was well polished with alumina powder on polishing cloth followed by washing in DD water and ethanol. The polished GCE was placed in a 0.1 M KCl solution containing 5 mM $TbCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$. Afterwards, 20 consecutive cyclic voltammetric scans were performed 0.8 to $-0.2V$ at a scan rate of 50 mVs^{-1} as shown in Fig. 1 (A). Then, the deposited electrode was rinsed with water and dried at room temperature. Consequently, the electrochemical polymerization of PEDOT over TbHCF/GCE was carried out in acetonitrile solution containing 1 mM EDOT and 10 mM $LiClO_4$ between -1 to 1.6V at a scan rate of 100 mVs^{-1} for successive number of deposition cycles (1, 2 and 3 cycles). Then, the prepared PEDOT@TbHCF/GCE was used in PBS (pH 5) for further electrochemical studies as shown in Scheme 1.

3. Results and discussions

3.1. Electrochemical mechanism in TbHCF deposition

The electrochemical deposition of TbHCF was achieved using cyclic voltammetry and displayed in Fig. 1 (A). It can be seen that $Fe(CN)_6^{3-/4-}$ shows the reduction and oxidation peaks at 0.24 and 0.33 V. The oxidation occurring at 0.54 V and reduction at 0.38 V indicate deposition of $K[TbFe(CN)_6]$, due to the chemical oxidation of Tb^{3+} ion and its complex formation reaction with $Fe(CN)_6^{4-}$ ion can be expressed by the following equations. The electrochemical reaction for the formation of TbHCF was similar to the previously reported MHCF [43].



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