Electrochemical oxidation of erythrosine at TiO$_2$ nanoparticles modified gold electrode — An environmental application

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ABSTRACT

In the present paper, TiO$_2$ nanoparticles were utilized to modify the gold electrode surface and to emphasize a useful technique for determination of a food dye, erythrosine. The utilized modifier was characterized by Scanning electronic microscopy (SEM), and X-ray diffraction (XRD) analysis. In the first portion of the work, the oxidation properties of the dye were examined at different pH ranging from 3.0–11.2, varying accumulation time and at different scan rates, by using the cyclic voltammetric technique. The number of electrons and protons involved in the reaction, and heterogeneous rate constant were calculated. The second portion of the work includes the appositeness of the estimated method for the detection of the dye in trace level by utilizing differential pulse voltammetric technique. In optimum conditions (supporting electrolyte pH, accumulation time, modifier amount) the peak current was proportional to the concentration in the range 0.1 μM–10.0 μM with detection limit 2.6 nM. The applicability of the proposed method was achieved for food industries as well as for environmental applications.

1. Introduction

Surface modification of electrode material has been a very important area in electrochemical research in recent years. In a glimpse, the fabrication concepts of the reported electrodes in electrochemistry, highlighted by their unique modified sensing surface, which is generally coated or bonded by a thin film of a selected material to offer the electrode with the attractive properties in a chemically designed manner. Nanoparticles play a unique role in the surface modification. Excellent size analogue when compared to nanoparticles are deficient in some of the physiochemical properties. In addition, the bioactivity of these nanoparticles also differs due to the surface properties such as energy level, electronic structure, and reactivity is different. Smaller size, contributing to the larger surface area per unit mass and higher catalytic activity has made most of the industrial and consumer products to use titanium oxide (TiO$_2$) nano particles largely [1,2]. In the visible and near infrared regions TiO$_2$ nanoparticles exhibit excellent optical transmittance [3,4]. TiO$_2$ is been used as a model transition metal vowed to its simple electronic configuration with empty conduction and filled valance band [5]. Further application of these molecules in electrochemistry [6–8] and sensor technology [9–12] as a surface modifier, has predominantly increased due to its

desirable surface properties and easiness to immobilize on the electrode surface.

In the category of food additives, synthetic food dyes are essential, to make the foodstuffs more attractive. The usage of synthetic colors is popular because of two reasons; one is they supplant their distinctive shade that cannot lost amid the mechanical procedures, and another one is maintenance of tactical color shade of the final product [13]. In any case, potential risks to human prosperity were caused by some of these substances. They induce unfavorable skin irritations in contact with a couple of drugs, and also produce carcinogenic effect [14]. Therefore, in food items, the use of synthetic colorants is controlled completely by various national legislations like World Health Organization (WHO).

Erythrosine (ERT) [2-(6-Hydroxy-2, 4, 5, 7-tetraiodo-3-oxo-xanthen-9-yl) benzoic acid], is one of the xanthene food dye (Fig. 1). Basically, it is utilized as a coloring agent for food and a host of different applications, for example, a dental plaque disclosing agent, a biological stain, printing inks, and cosmetics. As by the rule, the concentration range of erythrosine for food, by WHO is 0.01 mg/kg [15]. In humans and animals it causes different sorts of allergies, anemia, neurotoxicity, cancer-causing nature, thyroid issues, DNA harming actions, and xenoestrogen nature. Because of the perilous
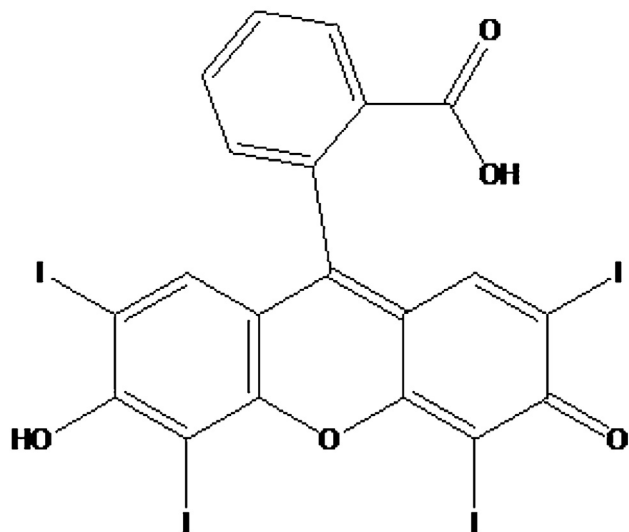
Fig. 1. Chemical structure of ERT.

nature and unsafe impacts of erythrosine, it was viewed as profitable to make an attempt to build up a straightforward strategy for the detection of erythrosine in various specimens.

A couple of methods were accounted for the detection of erythrosine, vowing to the significance of the dye. These consist of electrokinetic capillary chromatography, spectroscopy, high-pressure liquid chromatography (HPLC) and voltammetric methods [16–23]. Because of the high sensitivity, good precision, efficiency, time saving and simplicity of the experimental conditions, the electrochemical methods positioned high, compared to the other analytical methods. The redox behavior of the analyte can be acquired efficiently and effectively by the utilization of these methods [24,25]. Moreover, from the controlled modification of the sensing surface, new applications, intriguing properties and novel devices can be obtained.

There is a crevice in the literature, to understand the complete electrochemical activity of the dye erythrosine and the sensing effect of TiO_2 nanoparticles for dyes. Therefore the present work entirely concentrates on fabricating a responsive and prudent sensor to detect the electro-oxidation behavior and analytical applications of erythrosine based on the electro-catalytic activity of TiO_2 nano particles. Further, this proposed work was implemented for the investigation of analyte in pharmaceutical, biological and food samples for environmental application.

2. Experimental

2.1. Chemicals and reagents

The food dye, erythrosine (analyte), TiO_2 nanoparticles (modifier) and all other chemicals were purchased from Sigma-Aldrich. A solution of ERT (0.1 mM) was prepared by dissolving an appropriate amount of powdered sample in double distilled water. The effect of supporting electrolyte was studied by using 0.2 M phosphate buffer saline solution (PBS) of different pH ranging from 3.0–11.2 [26].

2.2. Instrumentation

An electrochemical analyzer (CHI Company, D630, USA) with three electrode system was used to study the voltammetric behavior of ERT at an ambient temperature. A gold electrode (GE) modified with TiO_2 nanoparticles serves as the working electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl (3.0 M KCl) as the reference electrode, respectively. The pH measurements were made by Elico pH meter model LI120.

2.3. Preparation of electrode

TiO_2 nanoparticles modified gold electrode (TiO_2/GE) was prepared by immobilizing TiO_2 nanoparticles on the surface of the gold electrode. TiO_2 nanoparticles suspension was prepared by suspending TiO_2 nanoparticles in acetone solution to give 1 mg/ml concentration. Prior to this, the surface of the electrode was cleaned by polishing the electrode surface on the micro cloth glued to glass using alumina of 3.0 μm size. The electrode was washed with ethanol to remove the alumina particles and then rinsed with double distilled water. The electrode was modified by pouring 1 μL of suspension on the surface of the electrode and air dried. The resulting electrode was been noted as TiO_2 nanoparticles modified gold electrode (TiO_2/GE).

The active surface area of the electrode was calculated by using Randles − Sevcik Eq. (1) and the surface area was investigated utilizing cyclic voltammetric technique, 1.0 mM $K_3Fe(CN)_6$ as a test solution and 0.1 M KCl as supporting electrolyte, at different sweep rates [27–29]. At T = 298 K and for a reversible process the equation is as follows:

$$I_p = (2.69 \times 10^5)\, n^{3/2}\, A\, D_0^{1/2}\, \nu^{1/2} C_0^* \tag{1}$$

The number of electrons transferred (n) during the electrode reaction is 1; the diffusion coefficient (D_0) is 7.6×10^{-6} $cm^2\,s^{-1}$ in Eq. (1). A refers to the sensing surface area of the electrode, C_0^* is the concentration of $K_3Fe(CN)_6$, Ip is peak current, ʋ is the scan rate. Hence, for the modified electrode, the surface area was found to be 0.154 cm^2.

2.4. Analysis of pharmaceutical tablets

The analysis was carried out using DPV technique. By utilizing a mortar and pastel, the ERT coated tablets were finely ground, and related weight with the stock solution were dissolved and diluted up to the mark in 100 mL volumetric flask. Proper dissolution was attained by sonication for ten minutes. While recording differential pulse voltammograms, the same conditions were maintained. Studies were accomplished by adding a known quantity of drug to pre-analyzed specimens.

2.5. Analysis of spiked human urine samples

Urine samples were obtained from two healthy volunteers and at room temperature (25 ± 0.1 °C) was centrifuged (4383 G) for 5 min. The obtained samples undergo two-fold dilution, using PBS of pH 4.2 and the test solution was prepared by spiking the filtrate with the known amount of ERT(0.1 mM).

3. Results and discussion

3.1. Characterization of TiO_2 nanoparticles

To understand the basics and performance of the modified electrodes, surface characterization of the modifier plays a very important role. The characterization of the modifier; TiO_2 nanoparticles was achieved by utilizing scanning electronic microscopy (SEM), and X-ray diffraction (XRD).

Fig. 2A.1 represents the SEM images of the TiO_2 nanoparticles, which describes the characteristic shape and size of the nanoparticles. The SEM image shows the spherical spongy module shaped particles, homogeneously distributed with aggregation.

The X-ray diffraction patterns of TiO_2 nanoparticles (Fig. 2A.2), shows as a function of reaction temperature. In the figure ten distinct peaks, equivalent to the (101), (004), (200), (105), (211), (204), (116), (220), (215), and (224) lattice planes, disclosing that the synthesized nanoparticles are in anatase form. By applying Scherrer equation the