

Determination of sunset yellow and tartrazine using silver and poly (L-cysteine) composite film modified glassy carbon electrode

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Silver and poly(L-cysteine) composite film modified glassy carbon electrode (PLC/Ag/GCE) has been fabricated via cyclic voltammetry and used for investigation of the electrochemical behavior of sunset yellow (SY) and tartrazine (TT). A pair of anodic peak at 0.760 V (vs. Ag/AgCl) and cathodic peak at 0.701 V (vs. Ag/AgCl) for SY and an anodic peak at 1.013 V (vs. Ag/AgCl) of TT are observed in pH 4.5 phosphate buffer solution. Based on the two well-resolved anodic peaks of SY and TT, a novel electrochemical method has been successfully developed for simultaneous determination of SY and TT using differential pulse voltammetry. Under the optimized experimental conditions, the linear range for the determination of SY and TT are 5.00×10^{-7} – 3.00×10^{-4} mol L⁻¹ and 7.50×10^{-7} – 7.50×10^{-4} mol L⁻¹, respectively with detection limits of 7.50×10^{-8} mol L⁻¹ and 2.50×10^{-7} mol L⁻¹, respectively. The proposed method has been applied for simultaneous determination SY and TT in beverage with satisfactory results.

Keywords: Analytical chemistry, Electroanalytical methods, Electrodes, Modified electrodes, Films, Composite films, Sunset yellow, Tartrazine

As an important food additive, edible synthetic colorants help in improving the appearance, color and texture of food and drinks, such as candy, fruit juice, carbonated beverage, etc. Unfortunately, synthetic dyes usually contain azo (N=N) functional groups and aromatic ring structures, which are harmful to human health¹. Hence, it is important to monitor and control the usage of the edible synthetic colorant in high consumption products. Currently, among the synthetic dyes, sunset yellow (SY) and tartrazine (TT) are the two most widely used synthetic pigments. Thus, developing a stable, sensitive and selective sensor for SY and TT has considerable significance for food inspection and guiding the dosage of edible synthetic colorant. Recently, many methods have been used to determine SY and TT, such as spectrophotometry²⁻⁵, electrochemical method⁶⁻⁹, high-performance liquid

chromatography^{10,11}, thin layer chromatography¹², photoacoustic spectroscopy¹³, etc. Due to the high sensitivity and simple operations, electrochemical method has achieved great development in the past several years. Ghoreishi *et al.*¹⁴ used gold nanoparticles carbon paste electrode to determine SY and TT; however, the linear range of their method was narrow. The glassy carbon electrode modified with metal silver is reported to improve the electrical conductivity of electrode and enhance the response signal to As(III) and Cr(VI)^{15,16}. Poly(L-methionine) modified glassy carbon electrode has realized simultaneous determination of acid, xanthine and hypoxanthine in human serum samples¹⁷. This illustrates that poly(amino acid) modified electrodes have a good catalytic effect on some organic molecules. Herein, silver and poly(L-cysteine) composite film modified electrode (PLC/Ag/GCE) has been prepared. The polymerized layer of L-cysteine covering the metallic silver reduces the dissolution loss of silver, because of which the stability of the electrode is improved. Moreover, PLC/Ag/GCE exhibits good sensitivity and precision toward SY and TT due to the synergistic effects of silver and poly (L-cysteine). Under the optimal conditions, a new method for simultaneous determination of SY and TT has been established and successfully applied to analyze beverage samples.

Experimental

Electrochemical experiments were conducted with a Zennium electrochemical workstation (Zahner, Germany). A three-electrode system was used for all electrochemical experiments, which consisted of an Ag/AgCl (saturated KCl) as the reference electrode, a platinum wire as the auxiliary electrode, a bare GCE (diameter 3.0 mm) or a modified electrode as working electrode. The surface morphology of electrode was observed with a scanning electron microscope (JEOL JSM-6610LV, Japan). All pH measurements were made on a PHS-3C digital pH meter (Shanghai Leici Device Works, China).

Sunset yellow, tartrazine, L-cysteine and silver nitrate were obtained from Sigma-Aldrich. All other chemicals used were of analytical grade. Doubly distilled water was used throughout the experiments.

Phosphate buffer solutions (PBS) were prepared with $0.1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4\text{-Na}_3\text{PO}_4$ and used as supporting electrolyte. All standard solutions and buffer solutions were stored in a refrigerator at $4 \text{ }^\circ\text{C}$, while all experiments were carried out at room temperature.

Before surface modification, a bare GCE was polished with $0.05 \text{ }\mu\text{m}$ α -alumina powder, until a mirror-like finish was obtained, and then sonicated with 1:1 HNO_3 solution, ethanol, and doubly distilled water in an ultrasonic aqueous bath for 5 min in sequence. The treated GCE was cyclic scanned from -0.9 to -0.1 V at a scan rate of 0.08 V s^{-1} for 8 cycles in a mixture containing $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ AgNO}_3$ and $0.5 \text{ mol L}^{-1} \text{ HNO}_3$. After modifying the surface of bare GCE with silver, the modified electrode (Ag/GCE) was electropolymerized by sweeping from 2.4 to -0.8 V at a scan rate of $0.14 \text{ V}\cdot\text{s}^{-1}$ for another 8 cycles in a solution with PBS ($\text{pH} = 4.5$) and $5.00 \times 10^{-3} \text{ mol L}^{-1}$ L-cysteine. After polymerization, the electrode was removed, rinsed thoroughly with doubly distilled water and air-dried. Finally, silver and poly(L-cysteine) composite film modified electrode (PLC/Ag/GCE) was successfully obtained.

Results and discussion

Figure 1 shows the SEM images of the surface of GCE, PLC/GCE, Ag/GCE and PLC/Ag/GCE. The bare GCE and PLC/GCE presents a smooth surface, while Ag/GCE has a rough and dotted surface. After the electrochemical polymerization of L-cysteine on Ag/GCE, PLC/Ag/GCE displays a roughness-lowered and dot-reduced surface. On observing the electrodes with naked eye, it is seen that Ag/GCE is covered with a silver-white film, while PLC/GCE and PLC/Ag/GCE have colored films. These details indicate that silver ions have been deposited and form metallic silver on bare GCE, while L-cysteine polymer is formed on both bare GCE and Ag/GCE.

Electrochemical impedance spectroscopy (EIS) is a valid method to characterize the features of a surface-modified electrode and can give information on impedance changes of the electrode surface during the modification process. The semicircle diameter at higher frequencies corresponds to the electron-transfer resistance (R_{ct}), while the linear part at lower frequencies is related to the diffusion process¹⁸. Figure 2 depicts the Nyquist plots of the EIS at GCE, PLC/GCE, Ag/GCE and PLC/Ag/GCE in the presence

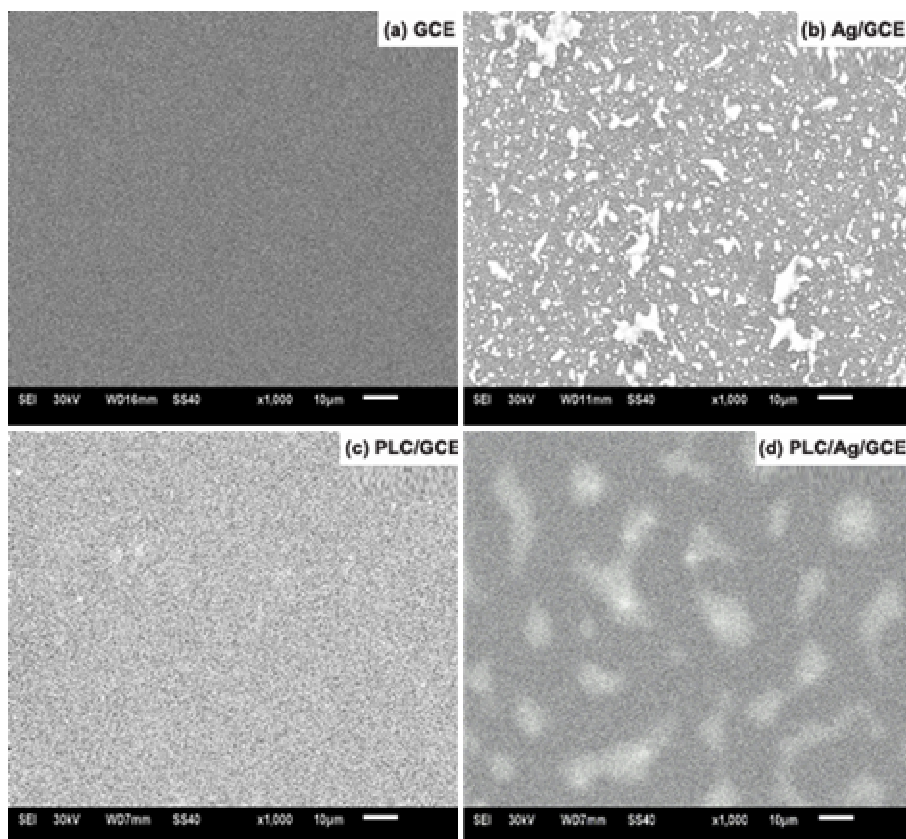


Fig. 1 — SEM images of (a) GCE, (b) Ag/GCE, (c) PLC/GCE and (d) PLC/Ag/GCE.

nitrogen through the solution. Each experiment was repeated six times (Table 3). The reliability of the present method was validated by analyzing SY and TT in the samples with an earlier reported electrochemical method²⁰. These data are also listed in Table 3. The results of the two methods were very close.

In conclusion, a novel modified glassy carbon electrode has been successfully fabricated via the construction of Ag and PLC film. The electrode exhibits good conductivity and high electrocatalytic activity for estimation of SY and TT. The anodic peaks of SY and TT were well separated by applying CV and DPV. The redox reaction of SY is mainly a absorption controlled process while the oxidation of TT is a diffusion controlled process. Owing to the excellent analytical performances of PLC/Ag/GCE, such as stability, reproducibility, selectivity and sensitivity, it can be used as a useful tool for simultaneous determination of SY and TT.

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