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Proceeding Paper

Voltammetric Sensors Based on the Mixed Metal Oxide Nanoparticles for Food Dyes Determination †

Guzel Ziyatdinova *, Liliya Gimadutdinova and Dar'ya Bychikhina

Analytical Chemistry Department, Kazan Federal University, Kremleyevskaya, 18, 420008 Kazan, Russia; liliya.gimadutdinova@gmail.com (L.G.); bychikhina02@gmail.com (D.B.)
* Correspondence: guzel.ziyatdinova@kpfu.ru

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Abstract: Synthetic dyes of various classes are widely applied in food production. Reliable and simple methods of dye determination are in demand for food quality control. Novel sensitive and selective voltammetric sensors based on glassy carbon electrodes modified with mixtures of metal oxide nanoparticles (NPs) dispersed in water or surfactant media have been developed for the first time for Sunset Yellow FCF, Brilliant Blue FCF, and Quinoline Yellow. Mixtures of CeO_2 and SnO_2 NPs dispersed in surfactants or CeO_2 and Fe_2O_3 NPs are the best sensing layers for the determining of Sunset Yellow FCF and Quinoline Yellow or Brilliant Blue FCF.

Keywords: voltammetry; transition metal oxides; nanoparticles; modified electrodes; synthetic dyes; food analysis

1. Introduction

Synthetic dyes of various classes are widely applied in food production due to bright and reproducible colors, high stability, and improvement of the foodstuff appearance [1,2]. The dye content in food is strictly regulated due to a wide range of possible negative health effects [3]. Therefore, simple and reliable methods are in demand for food quality control. The presence of electroactive fragments in the structure of synthetic dyes makes possible the development of voltammetric sensors for their quantification.

Voltammetric sensors are a promising tool for the fast screening of synthetic dyes of various classes due to high sensitivity and selectivity, reliability, low costs, and possibilities of application on-site [4–6]. The sensing layer consisted of various types of nanomaterials, and their composites were used to provide sufficient analytical characteristics of dyes. Metal oxide nanomaterials are among the effective electrode surface modifiers. Nanostructured cerium(IV), tin(IV), iron(III), neodymium(III), zirconium(IV), molibdenium(IV) oxides has been successfully applied as sensing layer of voltammetric sensors to synthetic dyes [5,7–11]. The combination of several metal oxides providing synergetic effect of each component is the further development in this field and shows improvement in the analytical parameters of the target dye analysis [12,13].

The current study is focused on the development of novel voltammetric sensors for Sunset Yellow FCF, Brilliant Blue FCF, and Quinoline Yellow based on a combination of metal oxide nanoparticles (NPs). Mixtures of cerium and tin dioxide NPs dispersed in cationic hexadecylpyridium bromide (HDPB) or non-ionic Brij® 35 surfactants have been shown to be the best sensing layers for the determination of Sunset Yellow FCF and Quinoline Yellow, respectively. The voltammetric sensor based on the mixture of cerium dioxide and iron(III) oxide NPs dispersed in water allows the determination of Brilliant Blue FCF. Sensors are characterized by scanning electron microscopy (SEM), electrochemical impedance spectroscopy and voltammetry.

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2. Materials and Methods

Sunset Yellow FCF (98% purity reagent), 85% Brilliant Blue FCF from Aldrich (Steinheim, Germany) and Quinoline Yellow from TCI (Tokyo, Japan) were used. Their stock solutions (1.0×10^{-3} M for Sunset Yellow FCF and Brilliant Blue FCF, 5060 mg L^{-1} for Quinoline Yellow) were prepared in distilled water.

CeO_2 and SnO_2 NPs as well as $CeO_2{\cdot}Fe_2O_3$ NPs were used as electrode surface modifier. The mixture of CeO_2 and SnO_2 NPs (1 mg mL^{-1}) was prepared from commercial reagents (10% CeO_2 NPs water dispersion from Sigma-Aldrich (St. Louis, MO, USA) and SnO_2 NPs powder from Aldrich (Steinheim, Germany)) using surfactant dispersive media. The standard 1.0 mM solutions of surfactants in water were prepared from the sodium lauryl sulfate (SLS) (Ph. Eur. Grade, Panreac (Barcelona, Spain), Brij® 35 (98%, Acros Organics (Geel, Belgium)), Tween® 80 (Merck, Steinheim, Germany), Triton X-100 and 98% HDPB from Aldrich (Steinheim, Germany). Dispersions of $CeO_2{\cdot}Fe_2O_3$ NPs (0.25–1.0 mg mL^{-1}) were prepared by exact dilution of 20% aqueous dispersion of $CeO_2{\cdot}Fe_2O_3$ NPs (50:50 wt.%) from Alfa Aesar Cerion (USA). Sonication for 10 min in an ultrasonic bath (WiseClean WUC-A03H) (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea) was applied for the NPs dispersion preparation. Then, electrode surface modification was performed using the drop casting method of 3–5 µL of NPs dispersion.

Electrochemical measurements were carried out at the potentiostat/galvanostat PGSTAT 302N with FRA 32M module (Metrohm B.V., Utrecht, The Netherlands) or PGSTAT 12 (Eco Chemie B.V., Utrecht, The Netherlands) with NOVA 1.10.1.9 software. GCE (3 mm diameter) from CH Instruments, Inc. (Bee Cave, TX, USA) or modified electrode, reference Ag/AgCl electrode, and auxiliary electrode (platinum wire) were placed in the electrochemical glass cell containing Britton-Robinson buffer (BRB) and cyclic or differential pulse voltammograms were recorded.

A MerlinTM high-resolution field emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany), operated at 5 kV accelerating voltage and a 300 pA emission current, was applied for the electrode surface morphology characterization.

3. Results and Discussion

3.1. Voltammetric Sensors Charcateristics

The voltammetric response of target dyes strongly depends on the sensing layer characteristics. The effect of modifier constituents (NPS and surfactants) and their concentrations has been tested. The mixture of CeO_2 and SnO_2 NPs in various surfactants as dispersive media has been studied. The nature of surfactants (anionic SLS, non-ionic Brij® 35, Tween® 80, and Triton X-100, cationic HDPB) and their concentration have been tested in the range of 0.050–1.0 mM have been tested. Anionic SLS cannot be used as a dispersive medium as far as promotes aggregation of NPs due to electrostatic effects. Non-ionic and cationic surfactants provide stable dispersions of CeO_2 and SnO_2 NPs. In the case of water dispersion of $CeO_2{\cdot}Fe_2O_3$ NPs, the effect of NPs concentration on the dye response has been evaluated. The electrode parameters that provide the best response of the target dyes are summarized in Table 1.

Table 1. Parameters of voltammetric sensors based on the mixed metal oxide NPs giving the best response to target synthetic dyes.

Synthetic Dye	Sensor	Modifier Concentration (mg mL^{-1})	V_{mod} (µL)	Surfactant Concentration (mM)	A (mm²)	k_{et} (cm s^{-1})
Quinoline Yellow	NPs CeO_2–SnO_2–Brij® 35/GCE	1.0	3	0.50	10.0 ± 0.2	4.43×10^{-4}
Sunset Yellow FCF	NPs CeO_2–SnO_2–HDPB/GCE	1.0	5	0.10	40 ± 2	1.58×10^{-3}
Brilliant Blue FCF	NPs $CeO_2{\cdot}Fe_2O_3$/GCE	0.75	5	0	70 ± 2	8.37×10^{-4}

The electroactive surface area of the sensors was evaluated using the electrooxidation of ferrocyanide ions in 0.1 M KCl. The data obtained (Table 1) indicate a significantly increased electroactive surface area vs. bare GCE (8.9 ± 0.3 mm^2). The electron transfer rate constant calculated on the basis of the charge transfer resistance obtained by electrochemical impedance spectroscopy confirms an 8.5–38-fold increase for the sensors based on the mixed metal oxide NPs compared to bare GCE.

The surface morphology of the created sensors has been studied by SEM (Figure 1). Spherical NPs are evenly distributed at the electrode surface forming porous coverage. Particles of average size of 28–90 nm with individual rhomboid inclusions are observed for NPs CeO_2–SnO_2–Brij® 35/GCE (Figure 1b). The NPs CeO_2–SnO_2–HDPB/GCE consisted of spherical NPs of 12–40 nm and of single aggregates up to 150 nm (Figure 1c). A fairly uniform porous coating of spherical particles with a diameter of 27-80 nm has been obtained for NPs $CeO_2 \cdot Fe_2O_3$/GCE (Figure 1d).

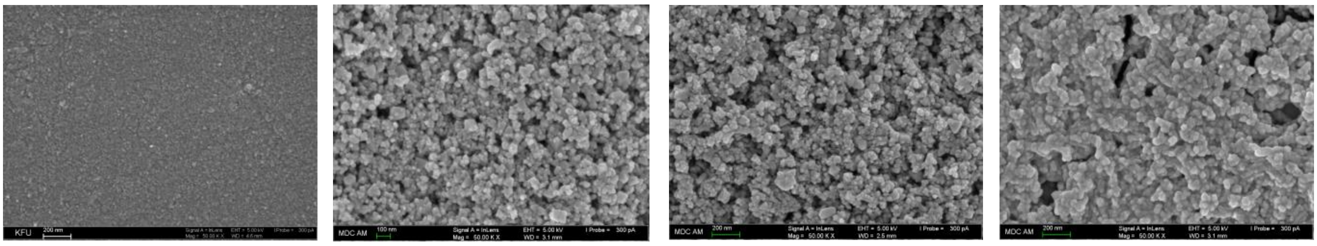

(**a**) (**b**) (**c**) (**d**)

Figure 1. SEM images of the sensor surface: (**a**) bare GCE; (**b**) NPs CeO_2–SnO_2–Brij® 35/GCE; (**c**) NPs CeO_2–SnO_2–HDPB/GCE; (**d**) NPs $CeO_2 \cdot Fe_2O_3$/GCE.

3.2. Synthetic Dyes Quantification

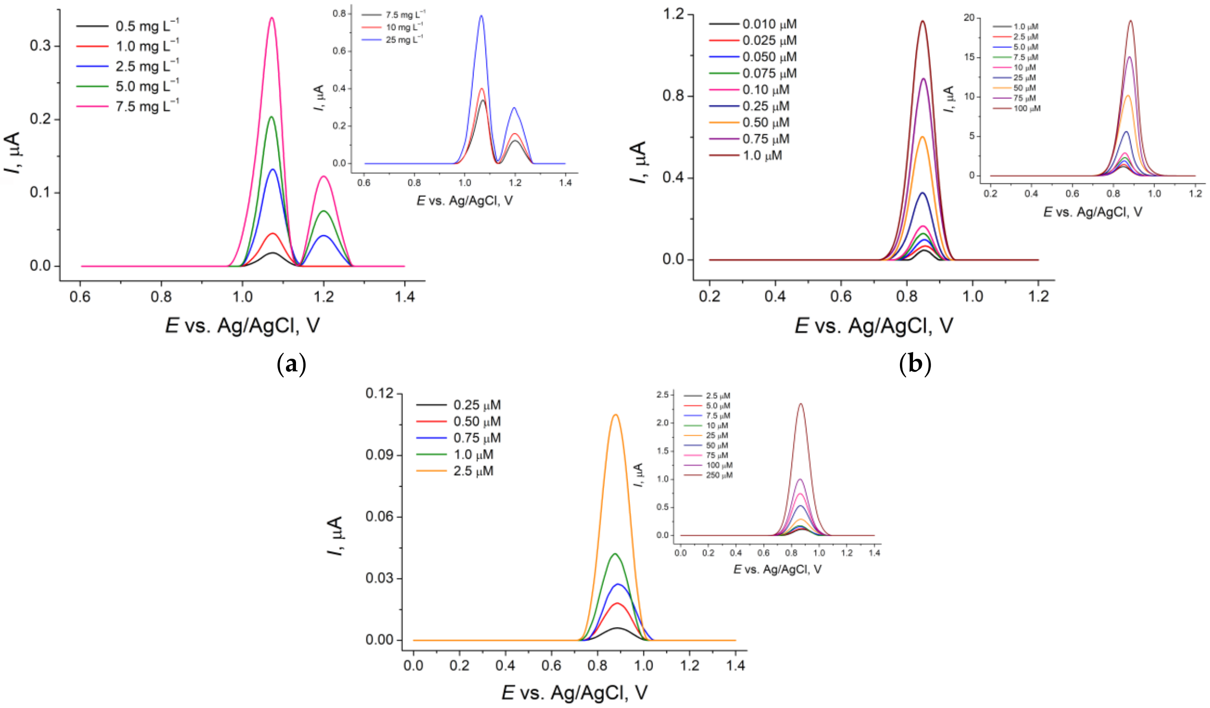
BRB was used as a supporting electrolyte in order to cover a wider range of pH. The changes in the voltammetric characteristics of dyes were studied. The highest oxidation peak currents were obtained at pH 5.0 for the Quinoline Yellow and Brilliant Blue FCF, and at pH 2.0 for the Sunset Yellow FCF.

Differential pulse voltammetry was applied for the quantification purposes. On the basis of dye oxidation peak current, the pulse parameters were optimized as modulation amplitude of 100 mV and modulation time of 25 ms for the Quinoline Yellow and Sunset Yellow FCF and modulation amplitude of 100 mV and modulation time of 75 ms for the Brilliant Blue FCF.

The oxidation peak current of all dyes (the first oxidation peak in the case of Quinoline Yellow) is linearly increased with the concentration growth (Figure 2). Two linear ranges have been obtained for each dye. The coefficients of determination of the corresponding linear plots are in the range of 0.9995–0.9998 confirming the high degree of sensors response linearity. The analytical characteristics achieved are presented in Table 2 which are improved vs. existing ones [8,13–19] and sufficient for application to real samples. Moreover, the absence of preconcentration step significantly simplifies the measurement and reduce its time.

Table 2. Figures of merit of the sensors based on the mixed metal oxide NPs for synthetic food dyes.

Voltammetric Sensor	Food Dye	E_{ox} (V)	Linear Dynamic Range	Detection Limit
NPs CeO_2–SnO_2–Brij® 35/GCE	Quinoline Yellow	1.07	0.50–7.5 and 7.5–25 mg L^{-1}	0.13 mg L^{-1}
NPs CeO_2–SnO_2–HDPB/GCE	Sunset Yellow FCF	0.85	0.010–1.0 and 1.0–100 μM	0.008 μM
NPs $CeO_2 \cdot Fe_2O_3$/GCE	Brilliant Blue FCF	0.86	0.25–2.5 and 2.5–250 μM	0.033 μM



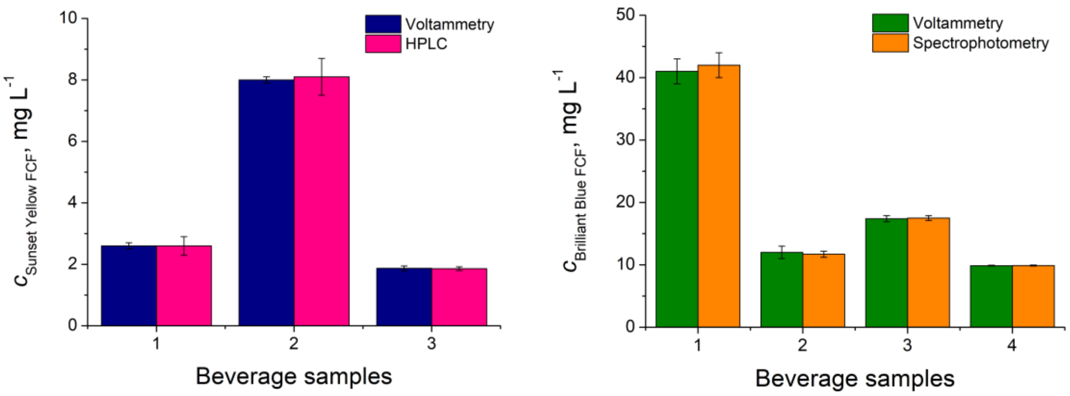
(**a**) (**b**)

(**c**)

Figure 2. Baseline–corrected differential pulse voltammograms of synthetic food dyes: (**a**) Quinoline Yellow at NPs CeO_2–SnO_2–Brij® 35/GCE in BRB pH 5.0; (**b**) Sunset Yellow FCF at NPs CeO_2–SnO_2–HDPB/GCE in BRB pH 2.0; (**c**) Brilliant Blue FCF at NPs $CeO_2 \cdot Fe_2O_3$/GCE in BRB pH 5.0.

The high accuracy of the developed sensors was confirmed by recovery of 99–100% in the model solutions containing target dye. The selectivity test in the presence of inorganic ions, carbohydrates, L-ascorbic acid, caffeine, as well as several other synthetic dyes typical for real samples was proven.

The developed sensors were applied in the beverages analysis. Sunset Yellow FCF and Brilliant Blue FCF were measured and their contents were compared with the data of the independent methods (Figure 3). A good agreement of the results obtained was observed. The corresponding *t*-test values of 0.205–1.18 and F-test values of 1.63–6.82 were less than the critical values indicated the absence of systematic errors and similar precision.



(**a**) (**b**)

Figure 3. Synthetic dye contents in the beverages: (**a**) Sunset Yellow FCF obtained by NPs CeO_2–SnO_2–HDPB/GCE and high–performance liquid chromatography; (**b**) Brilliant Blue FCF obtained by NPs $CeO_2 \cdot Fe_2O_3$/GCE and spectrophotometry.

4. Conclusions

Voltammetric sensors based on the mixtures of metal oxide NPs have shown a sensitive and selective response to synthetic food dyes of various classes. The data obtained allow to conclude that this type of electrode surface modifier is universal and can be considered as a perspective nanomaterial for organic electroanalysis. The simplicity of electrode surface modification opens perspectives of its fabrication using screen-printed technology, which can be used in combination with portable devices. Another direction of further development to be focused on the enlargement of metal oxide nanomaterials (nanoflowers, nanowires, nanoneedles, nanoribbons, etc.) including their mixtures as modifiers.

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