A Novel Electrochemical Nanosensor for the Simultaneous Sensing of Two Toxic Food Dyes

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ABSTRACT: This work reports for the first time the preparation and performance of a nanosensor for the simultaneous detection of metanil yellow and fast green, which are toxic food dyes. For the development of this sensitive platform, the surface of a glassy carbon electrode (GCE) was modified with calixarene and gold nanoparticles. The sensing ability of the designed nanosensor (calix8/Au NPs/GCE) was tested by cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy. The influence of a number of parameters was investigated for optimizing the conditions to achieve the best response of the target analytes. Due to the synergistic activity of calix[8]arene and Au nanoparticles, the calix8/Au NPs/GCE nano-composite was found to significantly enhance the signals of the selected food dyes in comparison to bare GCE. Under optimized conditions, limits of detection for metanil yellow and fast green were found to be 9.8 and 19.7 nM, respectively, at the calix8/Au NPs/GCE. The designed sensing platform also demonstrated figures of merit when applied for the sensing of food dyes in real water and juice samples. Moreover, high percent recovery, reproducibility, and stability suggested applicability of the designed electrochemical platform for real sample analysis.

1. INTRODUCTION

A number of synthetic dyes are illegally added into food items for imparting bright colors that render food more appealing for consumers. The dyes such as metanil yellow and fast green (FCF) are banned by food regularity authorities, but even then, these are added into a lot of food commodities, sauces, chili products, ice creams, soft drinks, and juices. The presence of toxic dyes in food products poses a serious threat to human health. For instance, the banned food additive metanil yellow is an established mutagen, which is classified as category II toxin by WHO. This dye is blamed for cancer development and damage to gastric mucin. Similarly, the prohibited food additive fast green has also been reported to inhibit the release of neurotransmitters and cause sarcoma, respiratory tract problems, and skin irritation. Despite these grave health problems, synthetic dyes are used in food products owing to their much lower price than natural dyes. Hence, for public health and quality control assurance, it is necessary to design sensitive analytical tools for monitoring the presence of toxins in food samples. In this regard, a number of analytical techniques such as high-performance liquid chromatography, gas chromatography–mass spectrometry, Raman spectroscopy, etc., are extensively used in food safety laboratories. However, complicated procedures, requirement of expert personnel, and comparatively higher cost have compelled the stakeholders to invest on the development of compact, simple, and efficient sensing devices that could offer a multitude of advantages in terms of precision, selectivity, robustness, easy fabrication, good sensitivity, minimal power requirement, specificity, reproducibility, and short analysis time. In this context, electrochemical sensors have emerged as analytical tools of ideal choice due to their improved selectivity, miniaturization, and high sensitivity.

Nanomaterials-based electrochemical sensors are an emerging class of sensing tools that find applications in environmental monitoring, food analysis, and disease diagnostics. Nanoparticles (NPs) of different sizes and shapes are mostly employed in the recognition layer of electrochemical sensors. Gold NPs are particularly used in electrochemical and colorimetric sensors due to their good electrical and optical properties. The binding propensity of Au NPs with suitable ligands is utilized for the preparation of active surfaces for sensing applications. After crown ethers and cyclodextrins, calixarenes are known as the most studied host systems. These are used in the preparation of stationary phases, ion transport membranes,
self-assembled monolayers, electrode ionophores, and sensors. Calixarenes are considered as nanobaskets. The macrocyclic cavity in their structure can encapsulate guest molecules. The functional groups in calixarenes can bind to molecules selectively via hydrogen bonding, specific stacking, or electrostatic interactions. Due to these unique features, calixarenes are used as electrode modifiers for enhancing the selectivity and sensitivity of the electrodes. In the present work, calix8 has been used as a component of the recognition layer by virtue of its electrode anchoring and host trapping abilities. Au NPs have been chosen as another component of the recognition layer because these can provide a high surface area and facilitate electron transfer between a wide range of electroactive species and electrode materials. Calixarenes are used in combination with gold nanoparticles as these act synergistically to impart the electrode with qualities of molecular recognition and efficiently respond to the redox events of target analytes. Keeping these features in consideration, GCE was modified with calixarene and gold nanoparticles (calix8/Au NPs/GCE). The designed electrochemical platform was used for the sensing of two food toxins: metanil yellow and fast green (see Scheme 1). The literature survey reveals that, so far, no report is available on the simultaneous detection of these food dyes. Hence, the current work is an effort to contribute in bridging this literature gap and to provide evidence-based information to the stakeholders of food safety laboratories.

2. EXPERIMENTAL SECTION

Metrohm Autolab PGSTAT302N was used for testing the performance of the designed electrochemical sensing platform, i.e., calix8/Au NPs/GCE. Experiments were conducted in an electrochemical cell using bare and modified GCE as the working electrode, platinum wire as the counter electrode, and Ag/AgCl immersed in saturated KCl solution (3 M) as the reference electrode. Analytical grade metanil yellow and fast green were obtained from Sigma-Aldrich (Darmstadt, Germany). The calixarene 8-hydroxy-8-propoxy-calix[8] arene was obtained from Fluka (Shanghai, China) and used as received. Gold nanoparticles (Au NPs) were synthesized by following the literature-reported method. Bare GCE was cleaned prior to every experiment for obtaining a suitable shining surface. For this purpose, the GCE was polished by rubbing with 0.05 μm alumina-water slurry over a rubbing pad to get a lustrous surface. To avoid grooving on the surface of GCE, it was rubbed in a manner of digit 8, which removed unwanted sticky particles. The electrode was then sonicated and rinsed thoroughly with a jet of doubly distilled water. The cleaned GCE was then subjected to several potential scans in the range of 0–1.4 V for achieving reproducible cyclic voltammograms. Modification of the GCE surface, a 3 mg/mL calix8 solution was prepared in DMF. A 5 μL droplet of this solution was put on the surface of GCE and dried under a drier. The as-prepared calix8/GCE was then rinsed with water for the removal of any loosely bound molecules of calix8. For immobilizing Au NPs, the calix8/GCE was kept dipped in the suspension of Au NPs for 20 min. The resulting electrode (calix8/Au NPs/GCE) was dried in an argon environment and applied for the detection of the selected food toxins, i.e., metanil yellow and fast green.

3. RESULTS AND DISCUSSION

3.1. EIS Using Bare and Modified GCE. The electronic transduction ability of the bare and modified electrodes was investigated in a solution containing 5 mM K3[Fe(CN)6] as a redox probe. EIS measurements were carried out in the frequency range of 1 Hz to 14 kHz at 10 mV amplitude. The obtained EIS data are shown in Figure 1A as Nyquist plots.

![Figure 1. (A) Nyquist plots using data obtained at unmodified and modified GCE with calix8, Au NPs, and calix8/Au NPs in a solution containing 5 mM K3[Fe(CN)6] as a redox probe. (B) Equivalent circuit model.](https://dx.doi.org/10.1021/acsomega.0c00354)

Figure 1. (A) Nyquist plots using data obtained at unmodified and modified GCE with calix8, Au NPs, and calix8/Au NPs in a solution containing 5 mM K3[Fe(CN)6] as a redox probe. (B) Equivalent circuit model.
An equivalent circuit model shown in Figure 1B involving a resistor, inductor, capacitor, Warburg impedance, and constant phase element was fitted to the experimental data. The parameters obtained from EIS data are listed in Table S1. The difference in the impedance parameters of the modified and unmodified GCEs points toward successful electrode fabrication. A gradual decrease in the charge transfer resistance value upon modification of the electrode surface with either gold nanoparticles or calix8/Au nanoparticles indicates faster charge kinetics on these modified electrodes due to reduction of the interfacial barrier to electron transfer as compared to bare GCE. The smallest value of $R_\text{ct}$ for calix8/Au NPs/GCE points to the enhanced electron transfer ability of these nanocomposites as compared to GCE modified with either Au NPs or calix8 alone. Thus, calix8/Au NPs/GCE was selected as the sensitive platform for the investigation of target analytes.

### 3.2. Voltammetric Analysis

#### 3.2.1. Differential Pulse Voltammetry of Metanil Yellow and Fast Green (FCF)

Differential pulse voltammetry (DPV), being a highly sensitive electroanalytical technique, is generally used to get the signals of analytes with enhanced resolution. Therefore, in the present work, DPV was used for recording of the voltammetric signatures of metanil yellow and FCF at bare and modified electrodes at a scan rate of 5 mV/s in the potential window of 0–1.2 V, keeping the pulse amplitude and width of 50 mV and 70 ms, respectively. An observation in Figure 2A,B reveals that metanil yellow and FCF oxidize at 0.58 and 0.84 V, respectively. Among the bare GCE, calix8/GCE, Au NPs/GCE, and calix8/Au NPs/GCE, the maximum current response can be noticed at calix8/Au NPs-modified GCE due to the synergistic contribution of Au NPs (highly electroactive surface area and good electrocatalytic activity) and calixarene molecules (host–guest complexation properties).

After ensuring the position of the oxidation signals of individual metanil yellow and FCF, both of these analytes were investigated simultaneously. The voltammetric response of a mixture of metanil yellow and FCF can be seen in Figure 3. The current intensities are maximum at calix8/Au NPs/GCE. These results are in good agreement with the EIS findings, as discussed vide supra. The role of calixarene and Au NPs can be considered like a stepping stone that facilitates electron transfer between the transducer and analytes. Upon application of the positive potential, the electrode is expected to attract electrons from the modifier and polarize its atoms. As a result, the modifier will attract electrons from the oxidizable moieties of the analyte and acceptor electrode due to application of the positive potential via a potentiostat. This interaction between the modifier and the dye results in enhancement of the signals of the respective dyes at the modified GCE by supporting host–guest interactions that lead to an increased concentration of the dyes near the vicinity of the electrode for enhanced voltammetric response, as is evident from the intense current signals shown in Figure 3. Hence, the analyte enrichment ability of the modified electrode is significantly greater than the GCE. A hopping mechanism of electron transfer between the dye molecules and the transducer is proposed in the presence of a multilayer mediator. In hopping electronic transport, the respective dyes on oxidation lose electrons to the polarized atoms of gold NPs as a consequence of the applied positive potential on GCE. These electrons may then transfer from atoms of Au NPs to acceptor sites on calixarene and eventually to the GCE.

#### 3.2.2. Cyclic Voltammetry

The voltammetric behavior of metanil yellow and FCF was also studied at various scan rates ranging from 25 to 250 mV/s. The information about signal intensity and scan rate can be related to either surface-assisted or diffusion-controlled electrochemical processes. Therefore, the effect of different scan rates on the anodic peak currents of metanil yellow and FCF was probed at calix8/Au NPs/GCE by cyclic voltammetry. The corresponding cyclic voltammograms are shown in Figure 4. The linear variation of the intensity of the peak current values with scan rate suggests surface-controlled oxidation of both metanil yellow and FCF on the surface of calix8/Au NPs/GCE (see Figure S1A). The plots shown in Figure S1B were obtained according to the following expressions

\[
\log I_p(\text{metanil yellow}) = 0.73 \log \nu - 4.62
\]

\[
\log I_p(\text{FCF}) = 0.63 \log \nu - 4.53
\]
The literature survey reveals that, if the slope of log of peak current as a function of log of scan rate is equal to 1, then the electron transfer mechanism is controlled purely by adsorption, whereas a value of 0.5 suggests a diffusion-controlled mechanism. In eqs 1 and 2, the slope values between 0.5 and 1 suggest that the electrode process involves contribution of both adsorption and diffusion of the analytes. However, adsorption is the dominant process, as depicted by the higher values of correlation coefficient of the plots of the peak current versus scan rate (Figure S1A) than the $R^2$ values of the plot of the peak current versus square root of scan rate (Figure S1C).

3.2.3. Condition Optimization. 3.2.3.1. Influence of Supporting Electrolyte, pH, and Accumulation Time. For condition optimization, the supporting electrolyte was examined first since it influences both the peak current and shape. Figure S1A,B demonstrates differential pulse voltamograms of a mixture of metanil yellow and FCF in different supporting electrolytes such as 0.1 M phosphate-buffered saline (PBS), acetate buffer, Britton–Robinson buffer (BRB), H$_3$PO$_4$, HCl, NaCl, and NaOH. The well-defined peak and higher current intensity demonstrate that 0.1 M PBS (pH 6.0) is the most suitable one among the tested supporting electrolytes. Thus, PBS was chosen for the investigation of the simultaneous sensing of target analytes for further studies.

To examine the effect of pH on the position and height of oxidation signals of metanil yellow and FCF, the pH of the solution containing PBS was varied from 5.0 to 8.0. An observation in Figure 6 reveals strong pH dependency of the signals of metanil yellow and FCF with a maximum peak height in a medium of pH 6.0. Figure S2A,B indicates the trend of $I_p$ and $E_p$ variation as a function of the pH values. The shift of peak potentials toward less positive values with an increase in pH suggests facile abstraction of electrons and protons at higher pH values.

Prolonging the accumulation time can increase the amount of dyes loaded onto calix8/Au NPs/GCE and lead to peak intensification, as shown in Figure S3A. The height of the peak significantly enhanced on extending the accumulation time from 5 to 70 s. The highest peak currents of metanil yellow and FCF at an accumulation time of 70 s suggest attainment of electrode surface saturation because further increase in accumulation time (see Figure S3B) showed no increase in current. Thus, the accumulation time of 70 s was chosen for analytical determination experiments (vide infra).

3.2.4. Analytical Application. 3.2.4.1. Calibration Plot and Limit of Detection. For the determination of the limits of detection of metanil yellow and FCF at the designed sensor calix8/Au NPs/GCE, DPV was carried out under optimized conditions of 70 s in 0.1 M PBS of pH 6. Figure 7A demonstrates concentration-dependent enhancement in Faradic signals of target analytes. Linear calibration curves in the concentration range of 0.05 to 45 μM were obtained for metanil yellow and FCF, respectively (Figure 7B,C). The limit of detection was measured using 3$\sigma$/m. The value of standard deviation $\sigma$ was calculated from the current values of the blank solutions at
shows that the voltammetric signals of these dyes at different concentrations each of Mg²⁺, Ca²⁺, Cd²⁺, Na⁺, Zn²⁺, and Cu²⁺ compared to the concentration of the dyes. Additionally, Figure S4C,D shows that the voltammetric signals of these dyes at calix8/Au NPs/GCE remain almost unchanged, with a very small current variation of less than 3% in the presence of 120-fold higher concentration of NO₃⁻, 25-fold higher concentration each of SO₄²⁻, CT⁻, and CO₃²⁻, and 10-fold higher concentration of glycine, alanine, sodium dodecyl sulfonate, and sucrose. These findings suggest good selectivity of the designed sensor for the detection of metanil yellow and FCF on the surface of modified GCE. Matching differential pulse voltammograms of 40 μM metanil yellow and FCF at the modified electrode prepared six times showed reproducibility of the designed sensing platform.

Table 1. Comparison of the Metanil Yellow- and FCF-Sensing Performance of the Designed Sensor with Reported Sensors

| Sr. no. | electrode substrate | dyes detected | measurement techniques | electrolyte | concentration range (μM) | LOD (μM) | ref |
|---------|---------------------|---------------|------------------------|-------------|--------------------------|---------|-----|
| 1       | calix8/Au NPs/GCE   | metanil yellow | DPV                    | PBS (pH 6)  | 0.05−45                   | 9.8 nM  | this work |
| 2       | calix8/Au NPs/GCE   | fast green FCF | DPV                    | PBS (pH 6)  | 0.05−45                   | 19.7 nM | this work |
| 3       | carbon quantum dots functionalized on GCE | metanil yellow | DPV                    | PBS (pH 5.4)| 0.06−40                   | 30.0 nM | 52   |
| 4       | sparked Mo-MoO₃ screen printed graphite electrode | simultaneous sunset yellow | DPV | 0.1 M acetate buffer solution (pH 5) | 5−250 nM | 2.0 nM | 53   |
| 5       | MWCNT/GCE           | sunset yellow FCF | DPV                    | 0.1 M PBS (pH 7) | 1.00−7.00 | 0.22 μM | 54   |
| 6       | MWCNT/GCE           | brilliant blue FCF | DPV                    | 0.1 M PBS (pH 7.0) | 65 | 55   |
| 7       | MWCNT/carbon paste electrode | brilliant blue FCF | DPV                    | PBS (pH 2.0) | 0.05−22 | 9.0 nM | 56   |

Table 2. Recovery Data of Metanil Yellow and FCF from Water and Juice Samples Using Calix8/Au NPs/GCE

| dye       | sample          | initially found (μM) | spiked amount (μM) | found (n = 3) (μM) | RSD (%) | recovery (%) |
|-----------|-----------------|----------------------|-------------------|-------------------|---------|--------------|
| metanil yellow | drinking water | 0                    | 50                | 48.5              | 1.20    | 97.0         |
|           | tap water       | 0                    | 50                | 49.5              | 1.18    | 99.0         |
|           | fruit juice     | 0                    | 70                | 66.5              | 1.05    | 95.0         |
| FCF       | drinking water | 0                    | 50                | 48.0              | 1.08    | 96.0         |
|           | tap water       | 0                    | 50                | 48.2              | 2.59    | 96.4         |
|           | fruit juice     | 0.5                  | 70                | 68 (expected = 70.5) | 2.96    | 96.4         |

4. CONCLUSIONS

A novel, robust, and efficient electrochemical sensor made up of GCE modified with calixarene and gold nanoparticles was prepared for the simultaneous detection of two prohibited toxic food dyes: metanil yellow and FCF. The components of the recognition layer significantly improved the oxidation signals of the dyes on the modified electrode surface as compared to unmodified GCE. EIS data offered evidence for the influence of the modifier in enhancing charge transfer of the redox probe through the electrode. Moreover, the role of the modifier for facilitating electron transfer between the guest (dyes) and the host (transducer) was ensured from the results of DPV. Conditions such as pH of the medium, accumulation time, and supporting electrolytes were optimized for getting intense current signals of the target food toxins at calix8/Au NPs/GCE. The designed sensor was found to display high sensing efficiency since it registered maximum current in less than 2 min. The sensor also showed figures of merit in the context of lower limits of detection for metanil yellow and FCF. Thus, the designed sensor is a promising new tool as no report is available until now for the simultaneous electrochemical sensing of both of these dyes. The nanocomposite sensor also showed reproducibility, wide linear range, and good selectivity for the selected food toxins. The results revealed practical applicability of the designed sensor for the determination of food toxins in real water and juice samples with high recoveries.
potential and peak current vs pH for metanil yellow and $E_p$ and $I_p$ as a function of pH for FCF; influence of accumulation time on the signal intensity of metanil yellow and FCF using calix8/Au NPs/GCE; DPV peak currents of 40 µM metanil yellow and FCF at the calix8/Au NPs/GCE; and parameters obtained from EIS data using various electrodes (PDF).

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**Notes**

The author declares no competing financial interest.

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