Electrochemical Detection of Melamine by Using Reduced Graphene Oxide–Copper Nanoflowers Modified Glassy Carbon Electrode

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ABSTRACT: In this work, a robust and reliable electrochemical sensor was developed for sensitive detection of non-electroactive melamine (MEL) using a modified glassy carbon electrode with ascorbic acid (AA) as the active recognition element. To increase the current signal of AA, the working electrode was successively modified with L-arginine (L-Arg) and reduced graphene oxide–copper nanoflower composite. The voltammetry measurements denoted that the hydrogen bonding was formed between AA and MEL. Using the optimum conditions, the proposed enhanced sensor can detect MEL concentrations ranging from $10 \times 10^{-9}$ to $9.0 \times 10^{-8}$ M with a detection limit of $5.0 \times 10^{-9}$ M that is proportional to the decrease of AA in the anodic peak current. Finally, the proposed sensor was successfully applied for the determination of MEL in commercial infant milk samples and good recovery values were obtained.

1. INTRODUCTION

Melamine (MEL) is a nitrogenous compound that is used in the production of glues, resins, laminates, adhesives, and plastics. Because of the presence of a high concentration of nitrogen (approximately 66%), MEL has been used as an adulterant in milk and milk powder industries. In 2007, a sequence of events related to MEL-contaminated animal feed and food occurred.1 Simultaneously, because of the expenditure of infant milk powder that contains MEL, some important incidents broke out such as acute renal failure, kidney failure, and death particularly among children. The formation of hyperplasia in the urinary bladder and bladder stones were associated with MEL exposition.2 The MEL toxicity was a source for kidney damage for extended time.3 MEL also produces an insoluble complex with cyanuric acid that results in subsequent tissue damage and crystallization such as urolithiasis.4 Therefore, it is necessary to develop robust and reliable methods for the sensitive detection of MEL for food sample monitoring.

For the detection of MEL concentration, various analytical methods such as high-performance liquid chromatography,5 enzyme-linked immunosorbent assay,6 ion-pair chromatography, capillary electrophoresis,7 and chromatography–mass spectrometry8 were developed. These analytical methods suffer from a diverse range of limitations including high-price equipment and/or reagents and time-consuming pretreatments. On the other hand, electrochemical methods are more advantageous because of their high sensitivity, simplicity in preparation and design, fast response, and low cost for detection of MEL. Unluckily, MEL has comparatively low electroactivity and good existence with 1, 3, and 5-triazine skeleton of the cyanamide trimmer. The electro-oxidation reaction of the amino group within MEL is responsible for its weak electrochemical response. For MEL detection, a few electrochemical methods were employed that have a low detection limit.10 Liao et al. used a disposable screen-printed electrode where uric acid (UA) was used as the recognition element.11 At the prepared electrode, the adsorptive behavior of MEL in the prepared electrode caused oxidation of UA. Furthermore, the decline in peak currents can be used for MEL sensing.12 Liu et al. developed an electrochemical sensor for the detection of MEL in milk using hexacyanoferrate and para-aminobenzoic acid as a molecularly imprinted polymer.13 In another report, Jin et al. used a graphite electrode with para-aminobenzoic acid to modify electrodes due to their excellent electrocatalytic properties.14,15 For instance, poly(L-arginine) can be spontaneously electro-
polymerized on the surface of electrodes for its significant outlook through the coalescence of $-\text{NH}_2$ and $-\text{COOH}$.

It was reported that poly(l-arginine) improves the electrode response stability and the analyte electroactivity. Inorganic nanoparticles incorporated with graphene oxide (GO) were reported to lead extraordinary function for electrode modification. Several other researchers observed the higher electrocatalytic performance of the modified electrodes using polymers and reduced GO (rGO) composites. The free amine group of polyarginine (P-Arg) can spontaneously be attracted to the carboxyl groups of GO. This provides an effective method for the detection of biomolecules. Song et al. used copper nanoflowers (CuNFs) such as the nanostructured electrode and observed excellent electrocatalytic activity in H$_2$O$_2$ sensing. Besides, CuNFs were reported to efficiently increase the electron transfer rate on the modified glassy carbon electrode (GCE) and used for glucose sensing.

In this paper, a novel one-step method is proposed for the preparation of CuNFs to incorporate with GO and jointly to be deposited on the GCE electrode for sensitive detection of MEL. The electrocatalytic activity of the bare and modified electrode is reported. Finally, the proposed sensor is used to detect different concentrations of MEL. Moreover, the commercial infant milk formula was analyzed with the proposed electrode to study the practical potential of the sensor.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials. All purchased chemicals were at their highest integrity. MEL, L-ascorbic acid, L-arginine, and GO nanosheets were purchased from Sigma-Aldrich (China) and were used without any further purification. Deionized (DI) water was used for the preparation of all solutions. The phosphate buffer solution (PBS) of 0.1 M was always used as an electrolyte solution, and the desired pH (6.0) was maintained by using diluted HCl.

2.2. Synthesis of CuNFs. A single-step hydrothermal method was used to synthesize CuNFs. At first, copper acetate monohydrate (600 mg) was mixed with 15 mL distilled water with vigorous stirring in a glass beaker. Separately, 1 g of polyvinylpyrrolidone was mixed with 108 mg D(+)-glucose and dissolved in 30 mL distilled water. Later, 1 M of sodium hydroxide solution was added dropwise to the main solution and immediately transferred in a Teflon-lined stainless-steel autoclave. The hydrothermal synthesis is conducted in a furnace at 140 °C for 14 h under atmospheric pressure. Finally, the residue was washed with distilled water/ethanol solutions for three times and dried in an oven.

2.3. Preparation of the GCE/P-Arg/ErGO–CuNFs Electrode. At first, GCE surfaces were polished with 0.05 μm of Al$_2$O$_3$ powder slurry on a polishing pad and ultrasonically rinsed with DI water for 2 min to remove alumina particles and other possible pollutants. The electrode was then washed ultrasonically in ethanol for 2 min and was allowed to dry. After careful polishing and washing, the electrode was immersed in 0.1 M of PBS (pH 7.0), containing 2.5 mM of l-Arg solution. An electrical potential ranging from $-2.0$ to $2.0$ V (at 100 mV s$^{-1}$ for 15 cycles) was applied by cyclic voltammetry (CV) for P-Arg deposition on GCE to obtain the GCE/P-Arg modified electrode. After electropolymerization, the electrode was allowed to dry in air. GO nanosheets were dissolved in PBS solution (1 mg mL$^{-1}$) and were then sonicated for 1 h. Later, 0.5 mg of freshly prepared CuNF powder was mixed with GO solution and the mixture was sonicated for 15 min. The ErGO-CuNF film was electrodeposited on the GCE/P-Arg electrode through cycling between $-1.4$ and $0.7$ V at 100 mV s$^{-1}$ for 15 cycles. The modified electrode was rinsed with DI water and dried carefully and denoted as the GCE/P-Arg/ErGO–CuNF-modified electrode.

2.4. Apparatus and Instruments. The electrochemical experiments were conducted in a three-electrode system using an electrochemical analyzer (CorrTest CS300, Wuhan, China). A GCE as a working electrode, silver/silver chloride (Ag/AgCl) as the reference electrode, and platinum wire (Pt-wire) as a counter electrode was used throughout the system. The morphology of nanomaterials was characterized by scanning electron microscopy (SEM) using a Hitachi S-3000H model, and transmission electron microscopy (TEM) was performed with the JEOL 2100 model.

2.5. Real Milk Sample Preparation. The infant milk powder was purchased from a local market. At first, 0.1 g of milk powder and 0.25 g of NaCl were dissolved in 10 mL of ultrapure water. Then, the obtained solution was ultrasonicated for 5 min and heated for 10 min at 100 °C. After that, the solution was centrifuged for 20 min at 4000 rpm and filtered using a filter paper. Finally, the solution was sufficiently diluted for analysis.

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization of CuNFs. The SEM and TEM measurements were performed to study the morphology and structural features of as-synthesized CuNFs with different magnifications. Figure 1a represents the uniform flower morphology of Cu nanoparticles with a diameter that ranges from 300 to 600 nm. TEM and high-resolution TEM were carried out, and the image is presented in Figure 1b. The uniform distribution of CuNFs is evidenced by the low-resolution TEM.
magnification image shown in Figure 1a. The length of the nanoflower is \textasciitilde 500 nm. The TEM image of a single nanostructure shown in Figure 1c reveals flower-like structures of the Cu particles with size and shape that are consistent with the observations obtained by the SEM images.

### 3.2. Electrodeposition of P-Arg and ErGO–CuNFs

CV was used for electrodeposition of P-Arg on the GCE electrode at a potential range from \(-2.0\) to \(2.0\) V with a scan rate of 100 mV s\(^{-1}\) for 15 cycles. Figure 2a shows the continuous deposition cycle of the P-Arg layer on GCE. During high positive potential, the monomer L-arginine oxidizes which stimulates the polymerization on an electrode surface and in agreement with results that were reported in an earlier study by our research group.\(^{22}\) The monomer of L-arginine can easily immobilize on the face of the electrode by the formation of a covalent bond (C–N). The electrodeposition of ErGO–CuNFs was performed by a series of CV from \(-1.4\) to \(0.7\) V (at 50 mV s\(^{-1}\) for 15 cycles), and GO–CuNF solution was dispersed in 0.1 M of PBS (pH 7.0) solution. The reduction of oxygen functionalities in GO can be observed from the first cycle with a large cathodic peak appeared from \(-1.0\) V.\(^{27,28}\) The electrodeposition of the conductive film over the electrode was confirmed by the increase in the peak currents with successive potential scans.\(^{29,30}\)

### 3.3. Electrochemical Behavior of the P-Arg/ErGO–CuNF-Modified GCE Electrode

The electrochemical characterization of the bare and modified electrodes was performed via CV in 0.1 M L\(^{-1}\) of KCl including 5.0 mM L\(^{-1}\) of Fe(CN)\(_6^{3−/4−}\); that is presented in Figure 3a,b. By looking at the figure, it can be seen that the lowest peak current with a pair of well-defined redox peaks was observed for bare GCE. The peak to peak separation (\(\Delta E_p\)) value was calculated as 276 mV for the bare GCE electrode, whereas the cathodic peaks increased with a \(\Delta E_p\) value of 197 mV after ErGO–CuNF modification which facilitated the electrochemical reaction of Fe(CN)\(_6^{3−/4−}\). It has been previously reported that the electron transfer kinetics correlates with the thickness of graphene film that can be easily control by the deposition cycle using the electrodeposition technique.\(^{31,32}\) Moreover, CuNFs effectively facilitated fast electron transfer between the modifying layer and GCE substrate because of its synergetic effect with the ErGO film. The electrochemical active surface
Figure 4. (a) Mechanism of MEL–AA complex formation. (b) DPV obtained in 0.1 M of PBS (pH 6.0) containing 1 mM of AA with and without the addition of $3.0 \times 10^{-8}$ M of MEL at a scan rate of 50 mV s$^{-1}$.

Figure 5. DPV's obtained for the determination of MEL using the GCE/P-Arg/ErGO–CuNFs electrode in a phosphate buffer (pH 6.0) at a scan rate of 50 mV s$^{-1}$ with a wide range of concentrations that varies from $1.0 \times 10^{-3}$ to $9.0 \times 10^{-9}$ M (a). The calibration curve for the measured concentrations (b).

The strong attraction of hydrogen atoms of AA and the nitrogen atoms of MEL form a new orbit in MEL–AA. The hydrogen atoms in molecular orbits can spontaneously move from the side of the molecular orbit. The presence of a large amount of $-\text{NH}_2$ and $-\text{OH}$ group in the MEL–AA complex makes the hydrogen bond stronger and more adequate. The stable configuration of the complex is responsible for the plane structure of MEL.$^{13}$

3.5. Electrochemical Detection of MEL. Figure 5 shows the differential pulse voltammetry (DPV) response of several MEL concentrations in 0.1 M PBS (pH 6.0) with the addition of a constant amount of $1.0 \times 10^{-3}$ M of AA. It was observed that the anodic peak current decreases proportionally with increasing concentration of MEL ranging from $10 \times 10^{-9}$ to $9.0 \times 10^{-8}$ M. A favorable linear relationship can be accomplished between the given MEL concentrations and the peak current. The linear regression equation is $y = -0.0363x + 5.3953$ ($R^2 = 0.9743$) with a detection limit of $5.0 \times 10^{-9}$ M. The obtained detection limit (S/N: 3) demonstrated that the GCE/P-Arg/ErGO–CuNFs sensor occupies a low detection limit and a broad linear concentration range.

We have compared our results with other methods for further investigation. Table 1 shows the properties of the modified GCE/P-Arg/ErGO–CuNFs sensor which indicates significant advantages including a low detection limit, acceptable linear range, and high sensitivity comparing to the other methods.

3.6. Selectivity, Reproducibility, and Stability Study. The selectivity of the developed sensor on the determination of MEL was investigated. The results revealed that more than 200-fold excess of Mg$^{2+}$, K$^+$, Ca$^{2+}$, Cl$^-$, SO$_4^{2-}$, and NO$_3$ had no any interference effect (<2%) to the determination of MEL. The negligible variation in the measured current in the
presence of such interference clearly indicates the high selectivity of the developed sensor toward MEL. To evaluate the reproducibility of the proposed sensor, a series of CV measurements were carried out. For a series of MEL measurements with the concentrations of 20 and 40 nM, the observed relative standard deviation (RSD) at n = 5 was 1.43 and 2.45%, respectively, which indicates excellent reproducibility. The modified electrodes were maintained at 4 °C for the stability test measurement, and the obtained peak current for 20 μM of analyte solution did not show an obvious change (lower than 5%).

3.7. Detection of MEL in Infant Milk Formula. A standard addition method was applied to the different portions of a real milk sample separately spoiled with different concentrations of MEL. A known amount of 4.0 × 10⁻⁸ and 8.0 × 10⁻⁸ M of MEL solution was added into 0.1 M of PBS (pH 6.0) and examined under optimum conditions. All samples experienced two collateral measurements. The experimental results are listed in Table 2 that suggests that the GCE/P-Arg/ErGO–CuNFs sensor occupies good recovery that ranges from 87.76 to 90.43% and an excellent reproducibility. Therefore, the modified GCE/P-Arg/ErGO–CuNFs electrode is considered efficient and reliable for the MEL detection in the milk sample.

4. CONCLUSIONS

We have successfully developed a simple GCE/P-Arg/ErGO–CuNF electrochemical sensor for the detection of MEL. The modified GCE/P-Arg/ErGO–CuNFs sensor was also reusable, and the response was reproducible. Therefore, this electrochemical sensor can be efficiently employed for MEL determination in food samples.

Table 1. Comparison of the Modified GCE/P-Arg/ErGO–CuNFs Sensor for MEL Detection with Other Methods

| methods                      | linear range (M) | detection limit (M) | references |
|------------------------------|------------------|---------------------|------------|
| Au/PANI NPs/GCE              | 0.1 × 10⁻³ to 1.0 × 10⁻⁷ | 1.39 × 10⁻⁹ | 34         |
| MIP–SPR sensor               | 0.1 × 10⁻³ to 1.0 × 10⁻⁷ | 9.87 × 10⁻⁹ | 35         |
| CNT–IL/MIP                   | 0.4 × 10⁻⁴ to 9.2 × 10⁻⁷ | 0.11 × 10⁻⁷ | 36         |
| poly/GCE                     | 4.0 × 10⁻⁴ to 450 × 10⁻⁸ | 0.36 × 10⁻⁷ | 37         |
| OMC/Naion/GCE                | 5.0 × 10⁻⁸ to 7.0 × 10⁻⁶ | 2.4 × 10⁻⁸ | 38         |
| MWCNT’s                      | 1.0 × 10⁻⁴ to 1.5 × 10⁻⁷ | 1.98 × 10⁻⁹ | 39         |
| DME’s                        | 1.0 × 10⁻⁴ to 6.6 × 10⁻⁸ | 3.0 × 10⁻⁷ | 40         |
| GCE                          | 1.0 × 10⁻⁴ to 5.0 × 10⁻⁸ | 3.0 × 10⁻⁷ | 41         |
| GCE/P-Arg/ErGO–CuNFs         | 1.0 × 10⁻⁴ to 9.0 × 10⁻⁶ | 5.0 × 10⁻⁹ | this work |

Table 2. Result of the Determination of MEL in the Real Milk Samples

| sample | added amount (M) | determined amount (M) | recovery (%) | RSD (%) (n = 3) |
|--------|------------------|-----------------------|--------------|-----------------|
| 1      | 4.0 × 10⁻⁴       | 3.62 × 10⁻⁸           | 98.85        | 1.4             |
| 2      | 8.0 × 10⁻⁴       | 7.02 × 10⁻⁸           | 90.26        | 1.2             |
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