



Analytical Methods

Determination of carbohydrates in honey and milk by capillary electrophoresis in combination with graphene–cobalt microsphere hybrid paste electrodes

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ABSTRACT

A graphene–cobalt microsphere (CoMS) hybrid paste electrode was developed for the determination of carbohydrates in honey and milk in combination with capillary electrophoresis (CE). The performance of the electrodes was demonstrated by detecting mannitol, sucrose, lactose, glucose, and fructose after CE separation. The five analytes were well separated within 9 min in a 40 cm long capillary at a separation voltage of 12 kV. The electrodes exhibited pronounced electrocatalytic activity, lower detection potentials, enhanced signal-to-noise characteristics, and higher reproducibility. The relation between peak current and analyte concentration was linear over about three orders of magnitude. The proposed method had been employed to determine lactose in bovine milk and glucose and fructose in honey with satisfactory results. Because only electroactive substances in the samples could be detected on the paste electrode, the electropherograms of both food samples were simplified to some extent.

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1. Introduction

As the products of photosynthesis, carbohydrates exist widely in honey, milk, fruits, grains, herbal drugs, beverages, wines, pharmaceuticals, etc. High performance liquid chromatography (Reinhold, Sheeley, Kuei, & Her, 1988), capillary capillary electrophoresis (CE) (El Rassi & Mechref, 1996), and microchip CE (Escarpa, 2014; Garcia & Escarpa, 2014; Suzuki & Honda, 2003) have been employed in their analysis. Because carbohydrates have neither chromophore nor fluorophore, they need to be derivatized prior to ultraviolet or fluorescence detection. Underivatized carbohydrates can be directly detected at platinum or gold electrodes using pulsed amperometric detection (Johnson & LaCourse, 1992; O'Shea, Lunte, & LaCourse, 1993). However, the applied potentials must be continuously pulsed to reduce the passivation of the electrodes during the detection. To solve these problems, cobalt (Cataldi, Casella, Desimoni, & Rotunno, 1992; Liu & Zheng, 2014), copper (Luo, Prabhu, & Baldwin, 1990), and nickel (Fermier & Colon, 1996) electrodes are employed in the AD of carbohydrates in alkaline mediums to minimize electrode fouling based on their electrocatalytic properties.

In the past decades, nanoparticles of copper (Chen, Zhang, & Chen, 2012), nickel (Garcia & Escarpa, 2011), NiO (Cheng et al., 2008) and CuO (Batchelor-McAuley, Du, Wildgoose, & Compton, 2008) were employed to fabricate detection electrodes for sensing carbohydrates in order to improve the sensitivity and anti-fouling capability of the electrodes. In addition, cobalt oxide nanoparticles were also prepared for the sensitive determination of carbohydrates owing to their unusual electrocatalytic properties (Ding et al., 2010; Kung, Lin, Lai, Vittal, & Ho, 2011; Sattarahmady & Heli, 2012).

Since Novoselov and Geim isolated and characterized graphene in 2004 (Novoselov et al., 2004), it has attracted tremendous scientific and technological attention because of its unique nanostructure and properties (Geim, 2011). Graphene has been used to fabricate electrochemical sensors and biosensors because of its excellent conductivity and electrocatalytic activity (Shao et al., 2010). To date, several approaches have been developed for the fabrication of graphene-based electrodes for electrochemical sensing. Among them, surface modification was commonly used (Han, Han, Shan, Ivaska, & Niu, 2010; Tang et al., 2009). In addition, graphene sheets were also modified on electrodes by electrochemical polymerization to fabricate electrochemical sensors (Feng et al., 2011). Recently, graphene–polymer composite electrodes were prepared by in situ polymerization for the amperometric detection

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(AD) of CE (Tang, Ma, Zhang, & Chen, 2013; Xu, Zhang, & Chen, 2013).

It has been demonstrated that electrically conductive graphene showed strong electrocatalytic activity when it was employed to improve the electrochemical response of some bioactive substances (Martin, Hernandez-Ferrer, Vazquez, Martinez, & Escarpa, 2014; Shao et al., 2010; Tang et al., 2013; Xu et al., 2013). The high electrical conductivity of graphene and its ability to promote the electron-transfer reactions indicate great promise for electrochemical sensing (Pumera, Ambrosi, Bonanni, Chng, & Poh, 2010). Because graphene sheets own large specific surface area, it is interesting to deposit cobalt particles on them for the sensitive detection of carbohydrates. However, to the best of our knowledge, no hybrid composed of metallic cobalt and graphene has been reported for electrochemical sensing of carbohydrates.

In this work, graphene–cobalt microsphere (CoMS) hybrid was prepared by the reduction of graphene oxide (GO) sheets and cobalt(II) chloride. The prepared hybrid was mixed with paraffin oil and packed into the ends of fused silica capillaries to form paste electrodes. The fabrication details, characterization, feasibility, and performance of the novel graphene–CoMS hybrid paste electrode have been demonstrated by determining carbohydrates in honey and milk in connection with CE in the following sections.

2. Experimental

2.1. Reagent and solutions

Graphite powder, potassium permanganate, sodium nitrate, cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), hydrazine hydrate (85% w/w), potassium borohydride, ammonium hydroxide solution (the content of NH_3 , 25–28% w/w), hydrogen peroxide solution (30% w/w), sulfuric acid (98% w/w), mannitol, sucrose, lactose, glucose, fructose, and paraffin oil were all supplied by SinoPharm (Shanghai, China). The separation medium for CE was 75 mM NaOH aqueous solution. The stock solutions (100 mM) of mannitol, sucrose, lactose, glucose, and fructose were prepared in doubly distilled water.

2.2. Preparation of graphene–CoMS and graphite–CoMS hybrid

In this work, a modified Hummers method was employed to prepare oxidized graphite (Chen et al., 2012). To prepare graphene–CoMS hybrid, 0.3 g oxidized graphite powder was dispersed in 100 mL doubly distilled water. The mixture solution was sonicated in an ultrasonic cleaner (SKQ-2200, frequency 56 kHz, 100 W) for 1 h to exfoliate oxidized graphite particles to GO sheets. After an aqueous solution (5 mL) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.19 g, 5 mmol) was added, the mixture was sonicated for 10 min. And then, 5 mL of hydrazine hydrate (85% w/w) and 10 mL of ammonium hydroxide solution (the content of NH_3 , 25–28% w/w) were successively added under violent stirring. The mixture solution was then heated in an 80 °C water bath for 10 min. To initiate the hydrazine-based reduction reaction, 20 mg potassium borohydride was directly dissolved in the mixture with the aid of mechanical agitation. It could be observed that the color of the mixture immediately turned from brown to black while a great deal of colorless gas released from the solution. After 60 min, the obtained graphene–CoMS hybrid was isolated by vacuum filtration and was purified by washing with copious amounts of doubly distilled water.

Graphite–CoMS hybrid was also prepared for comparison purposes. The preparation procedures and conditions were the same as those of graphene–CoMS hybrid except 0.15 g graphite powder was used instead of 0.3 g oxidized graphite powder. In addition,

graphene was prepared by the reduction of GO sheets with hydrazine hydrate as a reducing agent (Tang et al., 2013).

2.3. Electrode fabrication

The fabrication process of a graphene–CoMS hybrid paste electrode is shown in Fig. 1A–C. Graphene–CoMS hybrid powder was mixed with paraffin oil at a ratio of 3:1 (w/w). And then, a piece of copper wire (15 cm long and 150 μm diameter) was inserted into a fused silica capillary (320 μm I.D., 450 μm O.D., and 4.5 cm long) and a ~ 3 mm long opening was left for accommodating the paste. A drop of hot melt adhesive was applied to the other end of the capillary to immobilize the copper wire. Subsequently, the empty end of the capillary was inserted into the paste on a piece of glass plate. Note that the empty end of the capillary should touch the glass plate so that the paste could be pressed into the capillary until it touched the end of the copper wire in the capillary. Prior to use, the paste electrode was smoothed on a piece of weighing paper. Fig. 1D shows the photography of a typical CoMS hybrid paste electrode. The end of the copper wire is well buried in the packed hybrid paste. In addition, graphene paste electrode and graphite–CoMS hybrid paste electrode were also fabricated.

2.4. Apparatus

The CE-AD system used in this work has been previously reported (Tang et al., 2013). A high-voltage DC power supply (30 kV, Shanghai Institute of Nuclear Research, China) was employed to apply a separation voltage between the inlet and outlet of the capillary. The outlet of the capillary was maintained at ground. The electrophoretic separations were performed in a piece

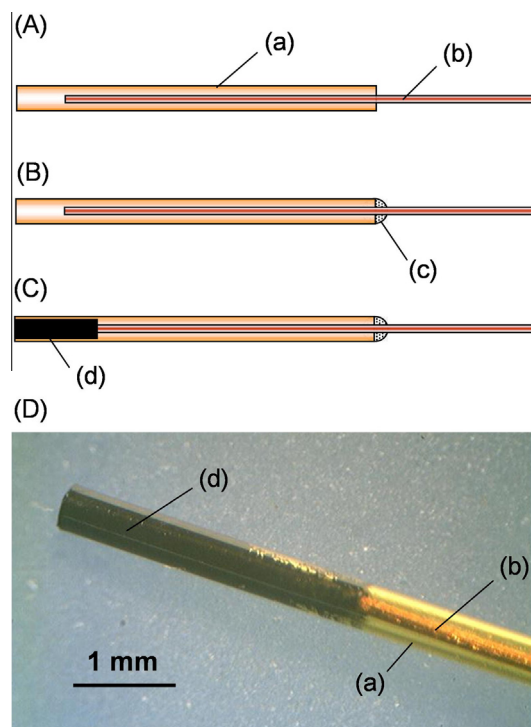


Fig. 1. Schematic illustrating the fabrication process of a graphene–CoMS hybrid paste electrode. (A) Inserting a piece of copper wire ((b) 10 cm long, 150 μm diameter) into a 3.5 cm long fused-silica capillary ((a) 320 μm I.D. \times 450 μm O.D.); (B) applying hot melt adhesive (c) to glue (b) in place, (C) filling the empty end of (a) with a mixture of graphene–CoMS hybrid and paraffin oil (3:1, w/w) (d), and (D) Microscopic photograph of a piece of graphene–CoMS hybrid paste electrode.

of fused silica capillary (25 μm I.D., 360 μm O.D., 40 cm long; Polymicro Technologies, USA).

The amperometric detection cell of CE contained a detection electrode, an Ag/AgCl wire reference electrode, and a platinum auxiliary electrode that were connected to a BAS LC-4C amperometric detector (Bioanalytical Systems Inc., West Lafayette, IN, USA). The detection electrode and the outlet of the capillary were aligned by a 3D adjustable device. The distance between the detection electrode and outlet of the capillary was adjusted to be $\sim 50\ \mu\text{m}$ (Chen et al., 2012).

CV was performed using a CHI 660D electrochemical analyzer (CH Instruments, Austin, USA) in combination with the three-electrode electrochemical cell mentioned above. A scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands) was employed to measure the scanning electron microscopy (SEM) images.

2.5. Sample preparation

Three honey samples (0.5 g each, purchased from local supermarkets) were each dissolved in doubly distilled water and diluted to 100 mL with doubly distilled water to prepare stock solutions. Prior to CE analysis, each solution was diluted with 75 mM NaOH at a ratio of 20 (1–20). To prepare the sample solution of bovine milk, 5 mL of bovine milk (Bright Dairy, Shanghai, China) was diluted to 100 mL with 75 mM NaOH aqueous solution. After vacuum filtration, the filtrate was diluted with 75 mM NaOH aqueous solution at a ratio of 20 (1–20) for subsequent CE analysis.

2.6. CE procedures

Before use, the separation capillary was rinsed with 75 mM NaOH aqueous solution for at least 10 min. Subsequently, the capillary was conditioned at a voltage of 12 kV between its two ends for 10 min. Both the separation and injection voltages were 12 kV. The detection potential was +0.60 V (vs. Ag/AgCl electrode). Sample solutions were injected electrokinetically at 12 kV for 6 s.

3. Results and discussion

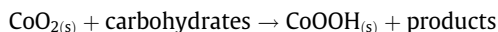
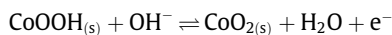
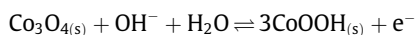
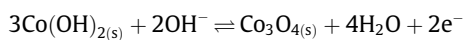
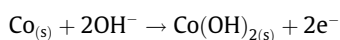
3.1. SEM images of CoMSs, graphene, and graphene–CoMS hybrid

The SEM images of CoMSs, graphene, and graphene–CoMS hybrid are illustrated in Fig. 2. In the absence of graphene, pristine CoMSs tend to aggregate (Fig. 2a). In comparison with the SEM image of graphene sheets (Fig. 2b), the crumpled silk waves-like morphology of graphene still exists in the graphene–CoMS hybrid (Fig. 2c). A great many of CoMSs can be observed on graphene sheets. The interconnected graphene–CoMS hybrid network is crucially important for electrical conduction. In this work, graphene–CoMS hybrid was prepared by the borohydride-initiated reduction of GO sheets and cobalt(II) chloride in a hydrazine-containing aqueous solution at a low temperature of 80 °C. The reaction time was 60 min. The average size of the CoMSs on graphene sheets is estimated to be $\sim 590\ \text{nm}$. Liang et al. prepared metallic cobalt–graphene composites through coprecipitation synthetic method followed by hydrothermal treatment at 180 °C (Wang, Wang, Hua, Zhu, & Liang, 2012). The time of hydrothermal reaction was 24 h. The metallic cobalt particles on graphene sheets possessed a maximum particle diameter of 300 nm. Obviously, the borohydride-initiated reduction approach allowed for the rapid and low-cost preparation of graphene–CoMS hybrid at a lower temperature and a lower pressure. The EDS spectrum of graphene–CoMS hybrid and the FT-IR spectra of graphene,

graphene–CoMS hybrid, graphene–CoMS hybrid, CoMSs, and GO are illustrated in Fig. A-1 (the details see Appendices).

3.2. Electrochemical oxidation mechanism of carbohydrates

Fig. 3 shows the cyclic voltammograms of a graphene–CoMS hybrid paste electrode, a graphite–CoMS hybrid paste electrode, and a graphene paste electrode in 75 mM NaOH aqueous solution containing 0 and 5 mM glucose. In the absence of glucose, two pairs of redox peaks are observed in the cyclic voltammograms of the graphene–CoMS hybrid paste electrode and the graphite–CoMS hybrid paste electrode (Fig. 3b and d) over the investigated potential range. Obviously, the current response of the graphene-based electrodes is much higher. The anodic and cathodic peaks found in the cyclic voltammograms of the cobalt-containing electrodes are in good agreement with earlier reports (Ding et al., 2010; Nakaoka, Nakayama, & Ogura, 2002). The anodic peaks at 0.25 and 0.60 V can be attributed to the $\text{Co(II)} \rightarrow \text{Co(III)}$ and $\text{Co(III)} \rightarrow \text{Co(IV)}$ redox transitions associated with different cobalt oxide species on the surface electrode (Casella, 2002). The cathodic peaks at 0.11 V and 0.50 V are related with the electrochemical reduction of the corresponding cobalt oxides formed in the positive cycles. As expected for an electrocatalytic oxidation process, a significant increase of the anodic peak at $\sim 0.60\ \text{V}$ and a considerable decrease of the cathodic peak at about 0.50 V are observed after the addition of glucose owing to Co(IV) species formed during the anodic sweep. However, no increase of the anodic peak at 0.25 V is found after adding glucose. The results indicate that there is no participation of the Co(II) and Co(III) species in the oxidation process and the electrochemically generated CoO_2 serves as the electrocatalyst for the oxidation of carbohydrates. The commonly recognized mechanism for the electrocatalytic oxidation of carbohydrates at cobalt(0)-containing electrodes in alkaline solution can be expressed as follows (Casella, 2002; Casella & Di Fonzo, 2011; Nakaoka et al., 2002),



The electrochemical oxidation of Co(0) generates the Co(IV) species on the CoMS-containing electrodes. In comparison with Fig. 3b and d, both the increase of anodic peak at $\sim 0.60\ \text{V}$ and the decrease of cathodic peak at $\sim 0.50\ \text{V}$ in Fig. 3a and c can be attributed to the reaction between Co(IV) species and glucose which rapidly converts CoO_2 to CoOOH (Ding et al., 2010). The current response at the graphene–CoMS hybrid paste electrode is much higher than that at the graphite–CoMS hybrid paste electrodes. Obviously, the CoMSs deposited on graphene sheets exhibit higher electrocatalytic activity toward the oxidation of glucose while graphene improves the electron transduction. The synergism between the CoMSs and graphene sheets in the hybrid can enhance the current response of carbohydrates significantly. As expected, there is no response of glucose on the graphene paste electrode in the absence of the cobalt constituent that is a crucial component for electrochemical of carbohydrates (Fig. 3e).

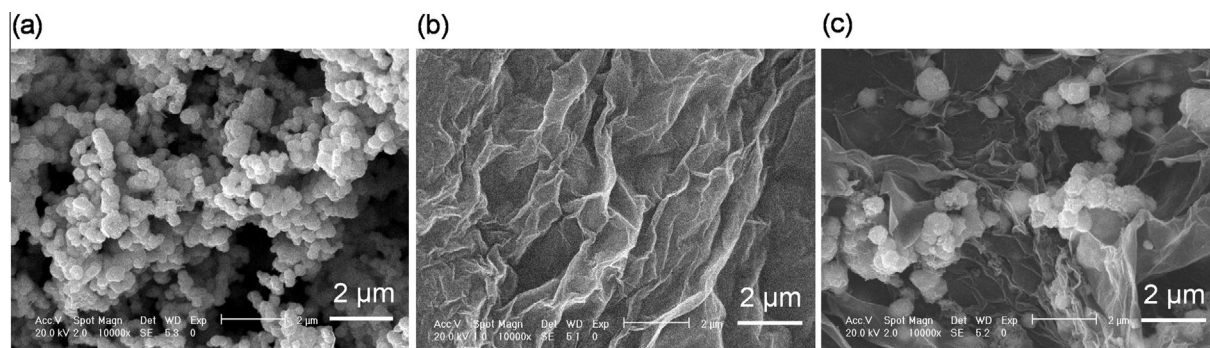


Fig. 2. SEM images of (a) CoMSs, (b) graphene, and (c) graphene-CoMS hybrid. Magnification, $\times 10,000$.

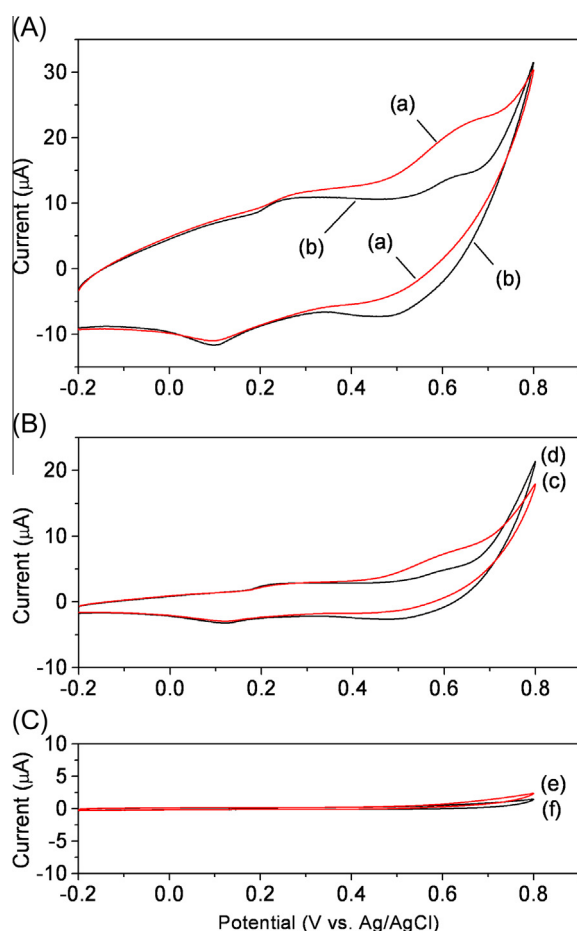


Fig. 3. Cyclic voltammograms at (A) a graphene-CoMS hybrid paste electrode, (B) a graphite-CoMS hybrid paste electrode, and (C) a graphene paste electrode (c) in 75 mM NaOH aqueous solution containing 5 mM (a, c, and e) and 0 (b, d, and f) glucose. Scan rate, 50 mV/s. The content of paraffin oil in the three pastes was 25% (w/w).

3.3. Detection potential

The cyclic voltammograms of mannitol, sucrose, lactose, and fructose (Fig. A-2 (the details see Appendices)) at the graphene-CoMS hybrid paste electrode are similar to that of glucose (Fig. 3a). When the applied potential is higher than +0.40 V, the oxidation currents of all the analytes increase rapidly. However, the peak current increase slowly upon increasing the detection potential above 0.60 V. Fig. 3b indicates that the background current of the graphene-based electrode increases

substantially when the potential is above 0.65 V. Considering the sensitivity and background current, a detection potential of 0.6 V was employed for the subsequent detection.

3.4. Linearity, detection limits, and half-peak widths

Fig. 4A illustrates the electropherogram of a mixture containing mannitol, sucrose, lactose, glucose, and fructose (0.25 mM each) at a graphene-CoMS hybrid paste electrode. The five analytes could be well separated within 9 min. A series of the standard mixture solutions of mannitol, sucrose, lactose, glucose and fructose (0.001–2.0 mM) were analyzed by CE in combination with the paste electrode. The linear equations between the concentration of the analytes (x , mM), the peak current (y , nA) were $y = 0.1083 + 285.185x$ ($R = 0.9997$, mannitol), $y = 0.1306 + 248.148x$ ($R = 0.9994$, sucrose), $y = 0.1251 + 219.453x$ ($R = 0.9992$, lactose), $y = 0.0938 + 297.219x$ ($R = 0.9995$, glucose), and $y = 0.1327 + 212.963x$ ($R = 0.9990$, fructose), where R was the correlation coefficient, respectively. Based on a signal-to-noise ratio of 3, the determination limits of mannitol, sucrose, lactose, glucose and fructose were evaluated to be 0.21, 0.24, 0.27, 0.20, and 0.28 μM , respectively. Because end-capillary amperometric detection was

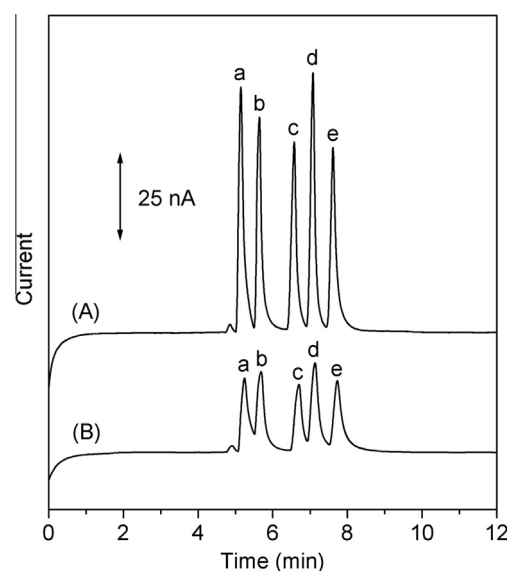


Fig. 4. Electropherograms for a mixture containing mannitol (a), sucrose (b), lactose (c), glucose (d) and fructose (e) (0.25 mM each) at (A) a graphene-CoMS hybrid paste electrode and (B) a graphite-CoMS hybrid paste electrode. Conditions: fused-silica capillary, 25 μm I.D. \times 40 cm long; electrophoretic separation medium, 75 mM NaOH; separation and injection voltage, 12 kV; injection time, 6 s; detection potential, +0.6 V (vs. Ag/AgCl electrode).

employed in this work, tailing peaks of these carbohydrates could be found in the measured electropherograms. These phenomena were observed in other CE-AD systems when nickel and copper were employed as the end-capillary detection electrodes (Fermier & Colon, 1996; Luo et al., 1990).

For comparison, a graphite-CoMS hybrid paste electrode was employed in the amperometric detection of the carbohydrates in combination with CE (Fig. 4B). The response of the five analytes at the graphite-CoMS hybrid paste electrode is much lower. It is well in agreement with the CV results (Fig. 3a and b). The sensitivities and detection limits were determined to be 85.185 nA/mM and 0.70 μ M for mannitol, 78.704 nA/mM and 0.76 μ M for sucrose, 75.092 nA/mM and 0.80 μ M for lactose, 93.518 nA/mM and 0.64 μ M for glucose, and 76.852 nA/mM and 0.78 μ M for fructose, respectively. The ability of the graphene in the hybrid to promote electron-transfer reactions on the electrode can be attributed to its special structure and high electric conductivity (Martin et al., 2014).

Moreover, broader peaks and inferior resolution were observed at the graphite-CoMS hybrid paste electrode (Fig. 4B). As illustrated in Fig. 4A, the sharp and well-resolved responses at the graphene-CoMS hybrid paste electrode resulted in smaller values of the half-peak widths for mannitol, sucrose, lactose, glucose and fructose relative to the graphite-based electrode (4.4 vs. 10.1, 4.9 vs. 9.0, 4.8 vs. 10.7, 5.1 vs. 9.9, and 5.8 vs. 10.9 s, respectively). Obviously, graphene in the hybrid paste electrode could also enhance the resolution of the five carbohydrates. It has been demonstrated that fast heterogeneous electron-transfer reactions on the detection electrodes of CE are essential for not only high sensitivity but also high separation efficiency (Pumera et al., 2010; Xu et al., 2013).

In a previous work, we determined mannitol, sucrose, lactose, glucose and fructose by CE in combination with a copper disc electrode (320 μ m diameter). The sensitivities of the four carbohydrates were in the range from 114.14 to 127.58 nA/mM (detection limits, 1–2 μ M), respectively (Chen, Zhang, Wu, & Ye, 2005). Obviously, the carbohydrates could be detected with higher sensitivity (212.96–297.22 nA/mM) and lower detection limits (0.21–0.28 μ M) when the graphene-CoMS hybrid paste electrode was used. In addition, the detection limits of the present electrode were also lower than those of pristine nickel electrode (1 μ M for sucrose, lactose, glucose, fructose, etc.) (Fermier & Colon, 1996).

3.5. Day-to-day and intraday reproducibility of detection

Nine determinations of a mixture containing mannitol, sucrose, lactose, glucose, and fructose (0.25 mM each) over 3 days (three times a day) resulted in the day-to-day signal reproducibilities of

3.9%, 4.6%, 4.2%, 4.9%, and 4.3%, respectively. The intraday reproducibility was examined from a series of nine repetitive injections of a mixture containing the five carbohydrates (0.25 mM each) under the selected conditions. The time of each run was 20 min. The relative standard deviations (RSDs) of peak current were 2.8%, 3.2%, 2.5%, 1.9%, and 3.7% for mannitol, sucrose, lactose, glucose and fructose, respectively. Such good repeatability reflects the satisfactory stability of the graphene-CoMS hybrid paste electrode. Because both paraffin oil and graphene are hydrophobic, they can prevent water from entering the paste electrode.

3.6. Electrode-to-electrode repeatability and alignment repeatability

To investigate the electrode-to-electrode repeatability, 20 pieces of graphene-CoMS hybrid paste electrodes were fabricated. They were coupled with the CE system for the amperometric detection of 0.25 mM glucose under the selected conditions. The average peak of glucose was measured to be 73.12 nA with a RSD of 8.4% ($n = 20$), implying that the electrode-to-electrode repeatability was satisfactory. Because the electrodes were prepared by packing the paste of graphene-CoMS hybrid powder and paraffin oil in uniform fused silica capillaries, the surface area and current response of the electrodes were satisfactorily reproducible among different electrodes.

In this work, a 3D adjustable device was employed for the alignment between the detection electrode and outlet of the capillary (Chen et al., 2012). A series of 15 repetitive measurements of 0.25 mM glucose was carried out by using a CE system coupled with a graphene-CoMS hybrid paste electrode that was aligned to the capillary outlet for each run. Reproducible peak currents were obtained with a RSD of 5.7%, indicating the satisfactory alignment of the detection electrode.

3.7. Sample analysis and recovery

The typical electropherograms of the diluted honey and milk are illustrated in Figs. 5 and 6. The determined contents of glucose and fructose in honey were 23.52% (w/w, RSD 2.7%, $n = 3$) and 37.50% (w/w, RSD 3.2%, $n = 3$) for sample 1, 28.59% (w/w, RSD 2.5%, $n = 3$) and 34.33% (w/w, RSD 3.6%, $n = 3$) for sample 2, and 24.17% (w/w, RSD 3.3%, $n = 3$) and 39.61% (w/w, RSD 2.6%, $n = 3$) for sample 3, respectively. They are well in agreement with the data in a previous report (23.9–33.0% for glucose and 35.7–45.0% for fructose) (Garcia & Escarpa, 2014). In addition, the content of lactose in the bovine milk was determined to be 48.47 g/L (RSD 2.9%, $n = 3$) that was close to the label value (4.8 g/100 mL).

Recovery experiments were carried out by adding accurate amounts of glucose, and fructose to a diluted honey in 75 mM

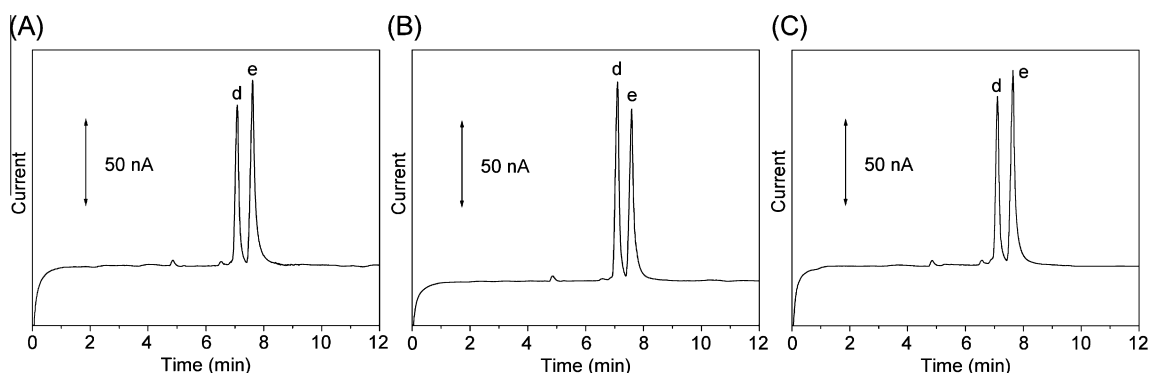


Fig. 5. Electropherograms of three diluted honeys ((A) Sample 1, (B) Sample 2, (C) Sample 3) at a graphene-CoMS hybrid paste electrode. Peak labels and conditions as in Fig. 4.

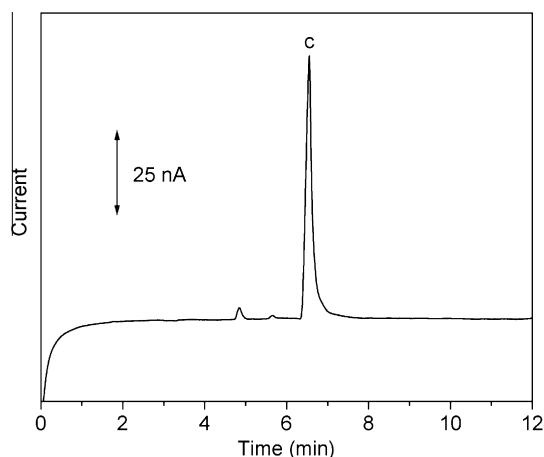


Fig. 6. Electropherogram of a diluted sample of bovine milk at a graphene–CoMS hybrid paste electrode. Peak labels and conditions as in Fig. 4.

NaOH aqueous solution. Subsequently, the standard-spiked sample solution was analyzed under the optimum conditions. The average recoveries and the corresponding RSD were measured to be 97.1% and 3.7% for glucose and 98.6% and 3.9% for fructose, respectively.

4. Conclusions

In summary, a novel graphene–CoMS hybrid paste electrode was successfully developed for electrochemical sensing of carbohydrates in bovine milk and honey. The performance, feasibility, and advantages of the novel detection electrodes have been demonstrated by the separation and detection of carbohydrates in combination with CE. It was demonstrated that CoMSs decorated on graphene sheets exhibited higher electrocatalytic activity toward the oxidation of carbohydrates while graphene improved the electron transduction. The synergistic effect significantly enhanced the current response of carbohydrates. The novel electrode offers favorable signal-to-background characteristics, sharp peaks for the carbohydrates as well as simple design and fabrication, indicating great promise for food analysis.

Conflict of interest

There is no conflict of interest in this work.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2015.05.059>.

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