2,5-dimethoxyaniline was electrochemically polymerized on glassy carbon electrodes, resulting in significant enhancement on the oxidation of glutamic acids. Differential pulse voltammetry of the thus-modification glassy carbon electrode revealed a 0.1 mM of D-glutamic acid solution generated two isolated peaks that were separated by more than 400 mV, indicating the feasibility of using this low cost and readily-to-fabricate platform for differentiating glutamic acid chiral molecules. Scanning electron microscopy measurements show that the in-situ synthesized 2,5-dimethoxyaniline polymer has a chain structure consisting of many nanometer size particles. Cyclic voltammetry experiments suggest that the oxidations of D- and L-glutamic acids are both charge-transfer controlled processes. Using cyclic voltammetry method, the anodic peak currents were found to have a linear relationship with the concentration of glutamic acids within the range between 0.5 and 15.0 mM, with a detection limit of 0.11 mM for L-glutamic acid and 0.26 mM for D-glutamic acid. The device-to-device reproducibility is great, confirming the robustness of this modification method. Consequently, there is a great need of distinguishing between right (D) and left (L) handed forms of molecules. However, detecting and quantifying chiral molecules remains challenging. A key step in sensing chiral molecules is to build a specific surface that can identify the differences between the enantiomers.11–15 Among the methods that have been developed for recognizing chiral molecules such as electrochemical,16–20 mass spectrometric,21–23 and spectroscopic,24,25 techniques, electrochemical detection is easier, faster and more economic than other methods. Polymer-modified electrodes have been increasingly used for chiral sensors in recent years,16–20 because the thickness, permeability and charge transport characteristics of the polymer film can be conveniently manipulated. For example, a chiral sensor toward L-phenylalanine was recently developed by electrochemically synthesizing poly[[2-(N-carbazolyl)ethyl methacrylate-co-methyl-acrylic acid] (PCEMMAs) on an ITO glass.26 Pandey et al. developed the molecularly imprinted polyaniline ferrocene sulfonic acid dots modified graphite electrodes by an electropolymerization method, which could be used to chiral separation of D-ascorbic acid and L-ascorbic acid.19 More recently, Borazjani et al. put forward a chiral sensor toward mandelic acid enantiomers by the electrochemical deposition of betamethasone, overoxidized polypyrrole and graphene nanosheet on a glassy carbon electrode.20

Glutamic acid is a key component in cellular metabolism, which influences the regulation of growth cones and synaptogenesis during the brain development and cognitive function such as learning and memorization.26,27 Relevant research also indicates that L-glutamic acid can increase the spontaneous release of dopamine through the direct control of nerve terminals by glutamatergic neurons.28 As a nutrient substance and flavor enhancer, glutamic acids can be found in all protein-rich plant foods (rice, wheat), dairy products, meats, poultry, even fish, eggs, etc. Therefore, the determination of glutamic acid is indispensable to ensure the quality of life. In addition to the time-consuming and complicated chromatographic and potentiometric titration methods,29–31 electrochemical detection using biosensors have also been explored in the last decade.32–34 Yet, there is no mention on differentiating D- and L-glutamic acids with these biosensors.

In the present work, 2,5-dimethoxyaniline (PDMA) was electrochemically polymerized at a glassy carbon electrode (GCE) and the thus-prepared PDMA-GCE was applied to oxidize small organic molecules such as D- and L-glutamic acids, hydrossine and pyrocatechol etc. Strong constructive interactions between PDMA and glutamic acids were observed, leading to the significant enhancement in the anodic current of glutamic acid oxidation. Importantly, two well-isolated anodic peaks can be seen in the differential pulse voltammetry of a D- and L-glutamic acid solution. The experimental results demonstrate that this low cost and easy-to-make platform can be potentially used to detect and differentiate glutamic acid enantiomers. The detection limit is 0.11 mM for L-glutamic acid using the cyclic voltammetry method.

**Experimental**

**Chemicals and apparatus.**—2,5-dimethoxyaniline (≥98%), sulfuric acid (95%-98%), and D-glutamic acid (DGA) were purchased from Aldrich. KCl (≥99%) was purchased from ACP chemicals Inc. L-glutamic acid (LGA) was obtained from Fluka A. G. Switzerland. Chloroform was purchased from Sigma-Aldrich. All solutions were prepared with double distilled water. A three-electrode system was employed for all the electrochemical experiments, including the synthesis of 2,5-dimethoxyaniline polymer. The bare or modified glassy carbon electrodes (3.0 mm in diameter) were used as the working electrode. Pt wire and a saturated calomel electrode (SCE) were employed as the counter electrode and reference electrode, respectively. All the electrochemical experiments were performed at room temperature (26 ± 1°C) with a CHI660D electrochemical workstation (CHInstrument, USA). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a Quanta 200 FEG microscope (FEI, Inc.). FTIR spectroscopy was performed...
by a Bruker ALPHA FTIR spectrometer using a platinum ATR sampling module.

FT-IR spectrum of the polymer is presented in Figure 1e, where the major features of the spectra are identical to existing reports on the (poly)2,5-dimethoxyaniline, providing further support on the formation of (poly)dimethoxyaniline, providing further support on the formation of (poly)dimethoxyaniline, providing further support on the formation of (poly)dimethoxyaniline. Aryl-methoxy C-O-C stretch peaks at 1200 and 1000 cm\(^{-1}\) arise from aromatic C-C stretch. Methoxy (aliphatic) C-H absorptions at around 3000 cm\(^{-1}\) are clearly observed in the spectrum, suggesting that methoxy groups remain in the PDMA.

**Results and Discussion**

**Electropolymerization of PDMA.**—Figure 1a displays the CV profiles recorded during the electrochemical polymerization of 2,5-dimethoxyaniline, where the electrolyte solution contained 10.0 mM 2,5-dimethoxyaniline and 0.5 M sulfuric acid. During the first forward scan from \(-0.2\) to 1.0 V (vs. SCE), only one anodic peak was observed at around 0.65 V, which corresponded to the oxidation of 2,5-dimethoxyaniline. On the reverse scan, a cathodic peak was observed at around 0.25 V. Notably, two new anodic peaks appeared at around 0.20 V and 0.34 V after the first cycle, presumably arising from the newly formed intermediates or oligomer of dimethoxyaniline on the GCE. The amplitudes of these two anodic peaks increased gradually with respect to the number of cycles, which was opposite to the oxidation peak of 2,5-dimethoxyaniline and was indicative regarding the continuous buildup of oligomer/polymer film at the electrode surface. Finally, after 30 cycles two anodic peaks were observed at around 0.2 V and 0.35 V with the cathodic counterparts around 0.34 V and 0.16 V, respectively. The above results suggest that the as-synthesized polymer itself could undergo redox reactions through two distinct stages.

Our experiments indicated that the electrocatalytic performance of PDMA-GCE platform could be further improved through a post-synthesis treatment in which the above prepared PDMA-GCE was subjected to 5 CV cycles in a 0.5 M H\(_2\)SO\(_4\) solution at a scan rate of 20 mV/s. In the absence of 2,5-dimethoxyaniline monomer, this post-synthesis treatment reduced oligomer/monomer content in the polymer matrix, making the polymer film chemically more uniform and stable. This chemical change is likely responsible for the observed improvement in the subsequent electrochemical detection of glutamic acids. Phenomenologically, after the polymerization reaction the bare GCE turned into a green color, which provided the first hand indication on the success of polymerization reaction. As opposed to the high solubility of 2,5-dimethoxyaniline monomer in chloroform, the synthesized polymer products do not dissolve in chloroform. The morphology of the PDMA film was characterized by SEM in Figure 1b, where the image indicated that the polymer had a chain structure consisting of many particles. The amplified SEM image in Figure 1c illustrated that these particles were in nanometer range. Figure 1d showed the surface of a bare GCE prior the polymerization reaction. Despite that the bare GCE surface was smooth and did not have any obvious defects and pits, the formed polymer film was nevertheless non-uniform, which might be related to the asymmetric molecular structure of the monomer. The emergence of so many polymer particles and chains provided ample number of active sites as well as increased surface area for mediating surface reactions. The CVs observed in Figure 1a are qualitatively the same as those seen during the electrochemical synthesis of (poly)dimethoxyaniline at a Pt electrode, leading us to postulate that the synthesized polymer has the same molecular structure as shown in the following:

**Electrocatalytic activity of PDMA-GCE toward D/L-glutamic acid oxidation.**—The electrochemical performance of the above modified electrode was investigated by both cyclic voltammetry and differential pulse voltammetry in Figure 2. Figure 2a presents the CV curves of the PDMA-GCE and bare GCE in a 0.1 M KCl solution containing 0.5 mM L- or D-glutamic acid. Comparing to the bare GCE, it is clear that the PDMA coating significantly enhanced the oxidation of glutamic acids, where a very strong anodic peak centred around 0.22 V could be seen for the L-glutamic acid. On the other hand, the D-glutamic acid showed a broad oxidation peak at about 0.61 V (vs. SCE). The above voltammograms indicate that the PDMA-GCE can be potentially used to differentiate D- and L-glutamic acid chiral molecules. Figure 2b presents a DPV of the PDMA-GCE in a solution containing 0.1 mM of L-glutamic acid and 0.1 mM D-glutamic acid. The supporting electrolyte is the same 0.1M potassium chloride
solution. As shown in Figure 2b, the voltammogram has two isolated peaks, which are separated by more than 400 mV. This result confirms the feasibility of differentiating D- and L-glutamic acid enantiomers. By spiking the above solution with L-glutamic acid while keeping D-glutamic acid concentration constant, one can quickly identify that the first peak corresponds to L-glutamic acid, while the second peak arises from D-glutamic acid. Unfortunately, the increase of L-glutamic acid concentration also caused a slight increase of the D-glutamic acid peak, making the simultaneous quantitative determination of the two isomers difficult. Nevertheless, the results shown in Figure 2 demonstrate that the two chiral molecules can be qualitatively differentiated here.

The oxidation kinetics of D- and L-glutamic acids at the PDMA-GCE were examined through cyclic voltammetry at various scan rates. Figure 3 plots the anodic peak current vs the scan rate, where a straight line with a linear correlation coefficient $R^2 > 0.998$ is obtained. When the peak current is plotted against the square root of the scan root, the linear correlation become much worse. The results suggest that for both D-glutamic (Figure 3a) and L-glutamic acid (3b), the oxidations are charge-transfer controlled.

Figure 4 shows the CVs of a PDMA-GCE in a solution containing various concentrations of (red) D-glutamic acid and (black) L-glutamic acid. The CVs illustrate that the peak current at this modified electrode increases proportionally when the concentration of D-glutamic acid is increased from 0.5 mM to 15.0 mM. The corresponding anodic peaks of L-glutamic acid are slightly higher than that of D-glutamic acid as shown, indicating that the PDMA film favors the oxidation of L-glutamic acid more than D-glutamic acid. Another noticeable difference was that the anodic peak shifted negatively as D-glutamic acid concentration was increased, whereas the anodic peak shifted positively in the case of L-glutamic acid. As shown in Figure 5, the PDMA-GCE had a linear response toward both D- and L-glutamic acid in the concentration ranging from 0.5 mM to 15.0 mM. The detection limits using the CV method is calculated to be 0.11 mM for L-glutamic acid and 0.26 mM for D-glutamic acid. The sensitivity is calculated to be 16.6 mM/μA for L-glutamic acid and 15.3 mM/μA for D-glutamic acid.

**Effects of PDMA property on the detection performance.** Properties of the electrochemically synthesized polymer may be affected by a number of parameters employed during the fabrication, such as the scan rate, potential window, and the number of cycles used. Such a property change was characterized here through the variation in their detection of glutamic acid. The effect of scan rates on the current responses of the PDMA-GCE toward glutamic acid was shown in Figure 6. Again, the polymer was synthesized in the solution containing 10.0 mM 2,5-dimethoxyaniline and 0.5 M sulfuric acid. As shown in Figure 6, the anodic peak currents of glutamic acid oxidation increased with the decrease of scan rates ranging from 100.0 mV/s to 20.0 mV/s. Such a trend is generally understandable, as the slow scan led to longer polymerization time and thus the possible increase of the PDMA film. However, the response current for L-glutamic acid decreased when being employed to detect D-glutamic acid, while the response current for L-glutamic acid increased slightly. The anodic peak potentials of the PDMA-GCE synthesized at 10 mV/s toward L- and D-glutamic acids showed no difference. The above results highlight that the differentiation of glutamic acid chiral molecules could be improved via optimizing the fabrication of PDMA. In this research, a scan rate of 20 mV/s has been selected for the preparation of PDMA-GCE.

**Figure 2.** (a) CV responses of the bare GCE and PDMA-GCE in a 0.1 M KCl solution containing 0.5 mM L-glutamic acid (1,3) or D-glutamic acid (2,4); and (b) DPV of the PDMA-GCE in 0.1 mM D-glutamic acid and 0.1 mM L-glutamic acid solution.

**Figure 3.** Plots of the oxidation peak currents against scan rates for (a) D-glutamic acid and (b) L-glutamic acid. The working electrode is PDMA-GCE.
As stated above, another parameter that affects the properties of PDMA-GCE is the number of cycles used for the polymerization. Increasing the number of cycles will increase the thickness of polymer, leading to different mass transportation behaviors. Figure 7 shows the anodic peak currents of the CV responses of the PDMA-GCE recorded in 15.0 mM D-glutamic acid and 15.0 mM L-glutamic acid solution, where the PDMA was synthesized with different number of CV cycles. As shown in Figure 7, the response currents increased firstly with the increment of the cycle numbers from 10 to 30, and then slight decrease was observed with 40 cycles and 50 cycles. Therefore, 30 CV cycles were used to synthesize polymer in this study.

Properties of the PDMA film can also be tuned through after-synthesis treatment. In this research we found that the catalytic activity of PDMA polymer could be further improved by the post-synthesis cyclic voltammetry treatment in a 0.5 M sulfuric acid solution. Figure 8 shows the CV responses of the PDMA-GCE synthesized with or without post-synthesis treatment toward 15.0 mM D- and L-glutamic acids. The results illustrate that the post-synthesis treatment in a 0.5 M sulfuric acid solution has increased the peak current.

Stability of the modified GCE and robustness of the modification method.—Stability of the PDMA-modified electrodes was tested by keeping the electrode in the air or in 0.1 M KCl supporting electrolyte at room temperature for several days. For the stability in air, the response current decreased about 4.5% after one day and 22.5% after two days. And then the response current became relatively stable for the following days. However, the modified electrode could only be kept stable for one day in the supporting electrolyte, where a decrease of 6.7% after one day and 82.10% after the second day were observed. While the stability of the modified electrode is disappointing, the same responses have been achieved with the PDMA-GCE that were prepared on different days or using different bare GCE electrodes. Such a result indicates the robustness of this modification method and provides a way to overcome its stability concern.

Mechanism of chiral recognition.—FT-IR measurements in Figure 1 suggest that the polymerization of 2,5-dimethoxyaniline takes place in the same way as aniline polymerization, where these benzene rings are connected through –NH+ centers. These –NH+ centers in the PDMA chain can interact strongly through coulombic attraction with the anions of glutamic acids (i.e., carboxyl anions in the molecule). It is known that when glutamic acids are added to water, they rapidly take on positive and negative charges simultaneously, assuming an electrically neutral zwitterion structure –OOC-CH(NH3+)-(CH2)2-COOH. The coulombic interaction between –NH+ centers and carboxyl anions is affected by the steric structures of the molecules involved, and the presence of two methoxy functional groups on the polymer chain provides a very specific spatial structure. CV responses shown in Figure 2 suggest that the PDMA matrix has a more suitable structure for stronger interactions with D-glutamic acid than with L-glutamic acid, resulting in a lower anodic peak potential of D-glutamic acid and the differentiation of the two chiral molecules. Figure 4 shows that the peak separation between D- and L-glutamic acids depends on their concentration, becoming less pronounced at a higher concentration. Such a complex behavior suggests that more investigations are needed in order to fully understand the underlying mechanism of the enhanced chiral sensing.
employed to oxidize several other mild reductants, such as hydro-
glutamic acid at the PDMA modified glassy carbon electrode.
Further experiments are needed to determine the oxidation process of
that the electrolytic oxidation of amino acids in sulfuric acid solution
one-electron oxidation of glutamic acid may occur at the amino group,
economic glutamic acid detector as well. According to literature,38 the
chiral molecules. The peak currents for both D- and L-glutamic acid
concentration was increased, the anodic peak potential of D-glutamic
mixture with a peak separation of more than 400 mV in the DPV. In
warrants better adhesion of the PDMA polymer film to the substrate.
2,5-dimethxyaniline on glassy carbon electrodes. The in-situ synthesis
been developed through the electrochemical polymerization of
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In this paper, a low-cost electrochemical sensor toward the
detection and differentiation of glutamic acid enantiomers has been
developed through the electrochemical polymerization of 2,5-
dimethxyaniline on glassy carbon electrodes. The in-situ synthesis
warrants better adhesion of the PDMA polymer film to the substrate. The PDMA-GCE could distinguish the L- and D-glutamic acid in a mixture with a peak separation of more than 400 mV in the DPV. In the CV measurements, anodic peaks of L-glutamic acid were slightly higher than that of the same concentrated D-glutamic acid. When their concentration was increased, the anodic peak potential of D-glutamic acid shifted negatively, as opposed to the slight positive shift of L-
glutamic acid, providing another reference for differentiating the two
chiral molecules. The peak currents for both D- and L-glutamic acid were found to increase linearly with their concentration in a range from 0.5 mM to 15.0 mM, suggesting the feasibility of using it as an economic glutamic acid detector as well. According to literature,38 the one-electron oxidation of glutamic acid may occur at the amino group, turning it into its corresponding cation radical. Studies also suggest that the electroolytic oxidation of amino acids in sulfuric acid solution produces the next lower aldehyde in the first step of the oxidation. Further experiments are needed to determine the oxidation process of glutamic acid at the PDMA modified glassy carbon electrode.

As part of the interference study, the PDMA-GCE has also been employed to oxidize several other mild reductants, such as hydroquinone, Na₂SO₃, malonic acid and nalidixic acid. The change of peak current was minimal when 1.0 mM of the above interferents were added to a 5.0 mM of glutamic acid solution. The results suggest that this easy-to-prepare PDMA has good selective toward the electrochemical oxidation of glutamic acids. Although the long term stability of the PDMA-GCE is a concern, the robustness of this modification method suggests that this new platform may be deployed for a low-cost screening of glutamic chiral molecules. The constructive influence of (poly)dimeethylamline is likely arising from two aspects: (1) it provides strong, but different for D- and L-, interactions with glutamic acids, facilitating their electrochemical oxidation; and (2) polymer itself evolves from the reduced leucoemeraldine to the oxidized pernigraniline forms at the high anodic potential, where the glutamic acids is oxidized to regenerate the reduced leucoemeraldine and lead to the enhanced anodic current. The detection limits using the CV method in a KCl solution is calculated to be 0.11 mM for L-glutamic acid and 0.26 mM for D-glutamic acid.

Conclusions

This research is supported by Natural Sciences and Engineering Research Council of Canada (NSERC), Li N. thank financial support from National Natural Science Foundation of China (21643015 and 11802025) and the Open Project (LHKE2014-C15) in the key Laboratory of Theoretical Chemistry of Environment, Ministry of Education. Xin Zeng thanks China Scholarship Council for the scholarship (Student ID: 201706030032).

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