Direct determination of oxalic acid by a bare platinum electrode contrasting a platinum nanoparticles-modified glassy carbon electrode

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\textbf{ABSTRACT}

A bare platinum disk electrode without further decoration was directly used to determine oxalic acid (OA), showing good linear ranges of $0.57$–$104.01 \ \mu M$ and $104.01$–$228.75 \ \mu M$ with a low detection limit of $0.38 \ \mu M$ (S/N = 3). In contrast, platinum nanoparticles (PtNPs) dispersed on a glassy carbon electrode were successfully achieved by an one-step electrochemical deposition method, possessing relatively wider linear detection ranges of $1.14$–$342.80 \ \mu M$ and $342.80$–$548.92 \ \mu M$ for OA with a lower detection limit of $0.28 \ \mu M$ (S/N = 3). Both the proposed electrochemical sensors exhibit great reproducibility, stability and selectivity. In particular, they have been applied to the determination of OA in real spinach samples, showing excellent analytical performance.

\textbf{1. Introduction}

Oxalic acid (OA), the simplest dicarboxylic acid, widely exists in plants, animals and microorganisms. According to incomplete statistics, only 8 of 113 plants do not contain OA and the average content of OA accounts for 6.3% of plant dry weight.\cite{ref1} Certainly, OA occurs in spinach, ginger, tomato, chocolate and so forth and in forms of less soluble salts such as Ca\textsuperscript{2+}, Fe\textsuperscript{2+}, Na\textsuperscript{+}, Mg\textsuperscript{2+} or K\textsuperscript{+}. High levels of these insoluble salts in diet can lead to irritation of the digestive system, especially the stomach and kidney.\cite{ref2} Normally, urinary excretion of OA does not exceed 40 mg per day in adults.\cite{ref3} By contrast, the content of blood OA is even lower, usually ranging from 6.70 to 25.60 \ \mu M in normal human serum.\cite{ref4} Consequently, the daily intake of OA from diet should be monitored and kept at a permissible level. For example, the OA content of spinach is listed as 9.70 mg per 1 g serving by the U.S. Department of Agriculture (USDA).\cite{ref5} Therefore, establishing a more effective and simple method of determining OA in practice is of great significance.

Numerous methods have been reported to detect OA, such as high-performance liquid chromatography,\cite{ref6} co-electroosmotic capillary electrophoresis,\cite{ref7} flow injection...
spectrophotometric,[8] ion chromatography,[9] chemiluminescence[10] and enzyme-based biosensors.[11] However, some of these techniques suffer from time-consuming manipulations, requirement of comparatively expensive equipment and insufficient long-term stability for enzyme activity. OA determination by electrochemical sensing has recently received extensive attention due to its low cost, low limit detection and rapid analysis.[12,13] Electrode materials used for these sensors include boron-doped diamond electrode,[2] carbon nanotubes-modified electrode [14] and so on. However, the oxidation of OA at these electrodes demands higher oxidation overpotential. In contrast, platinum electrodes show excellent electrochemically catalytic properties towards OA oxidation with a relatively lower oxidation overpotential.[15,16] Most of OA sensors based on platinum have focused on platinum nanoparticles (PtNPs) immobilised nanocomposites, which are more active than bulk platinum because of larger surface areas of loaded PtNPs and high conductivity of support materials.[17,18] However, the formation of these PtNPs nanocomposites with supporting nanostructures is usually a multiple-step process and it would complicate the preparation of electrodes, potentially causing the proposed sensors unstable. As mentioned previously, electrochemical oxidation of OA using a bare Pt electrode is obvious and straightforward, but no attention has been given to this old-fashioned method for electrochemical sensing of OA alone. Thus, the difference of electrochemical OA determination by a bare Pt electrode and a PtNPs-modified glassy carbon electrode (PtNPs/GCE) needs to be investigated.

In order to achieve the maximum potential of a bare Pt electrode for OA determination, constant potential amperometry has been utilised in this work. As a comparison, a PtNPs/GCE by electrochemical deposition with cyclic voltammetry (CV) is also prepared. Both modified and unmodified electrodes show wide linear detection range and low detection limit for OA. Moreover, avoiding complicated electrode preparation processes, both resulted electrodes display excellent stability, reproducibility and selectivity for OA determination. Finally, the proposed OA sensors were successfully used in the quantitative determination of OA in real spinach samples and the results were in conformity with the value served by USDA, confirming the availability of these electrochemical sensors.

2. Experimental

2.1. Chemicals and reagents

Perchloric acid (analytical grade) was purchased from Guangzhou Chemical Reagent Factory. Oxalic acid was obtained from Yueqiao Reagent Plastic Co., Ltd., Taishan, China. Hexachloroplatinic acid hydrate (H₂PtCl₆·6H₂O) was received from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All other reagents were of analytical grade and used without further purification. PBS (0.02 M, pH 7.4) was prepared by mixing the solution of NaCl, Na₂HPO₄ and NaH₂PO₄. Water used in all experiments was doubly distilled.

2.2. Apparatus and method

The scanning electron microscopy (SEM) image was determined with a JEOL JSM-6701F at an accelerating voltage of 5 kV. Energy dispersive X-ray spectroscopy (EDX, JEOL
JSM-6701F) was used to determine the chemical compositions of the prepared nanomaterial on a GCE at an accelerating voltage of 20 kV. All electrochemical measurements were carried out on a CHI 660D electrochemical workstation (Shanghai Chenhua instrument Co., Ltd., China), and with a conventional three-electrode system. In the experimental process, a bare platinum electrode and a platinum nanoparticles modified GCE were served as the working electrodes. A saturated calomel electrode and a platinum wire electrode were used as the reference electrode and the counter electrode, respectively.

The calculation method of detection limit was based on the 3sigma method [19] by the linear calibration plot.

\[
\text{Limit of detection (LOD)} = 3\sigma/s
\]

where \(\sigma\) is the standard deviation of difference value of adjacent points of y-coordinates from linear calibration plot (current versus OA concentration), and \(s\) is the slope of the calibration line, that is, the sensitivity.

### 2.3. Electrodes and samples preparation

Bare GCEs (3 mm diameter) and bare platinum electrodes (3 mm diameter) were polished to a mirror-like surface sequentially with 1-, 0.3- and 0.05-μm micron aluminium oxide powder, and ultrasonically washed with acetone, ethanol and doubly distilled water. Bare platinum electrodes were scanned from \(-0.3\) to \(1.3\) V by CV for 50 cycles at a scan rate of \(1\) V s\(^{-1}\) in 0.1 M sulphuric acid solution prior to use. Electrodeposition of PtNPs on GCE was carried out in 1 mM H\(_2\)PtCl\(_6\), 20 mM HCl and 0.02 M PBS (pH 7.4) with CV scan ranging from \(-0.4\) to \(0.6\) V at the scan rate of 100 mV s\(^{-1}\) for 125 cycles at room temperature under deoxygenated atmosphere with high purity (99.999%) nitrogen.

Spinach (100 g) was cut into small pieces, pounded in an agate mortar and extracted with 300 mL of water and heated at 85°C for 2 hours. Afterwards, the spinach sample was cooled down to room temperature and filtered twice through a filter paper with 100 mL of water. The obtained residue was centrifuged at 3000 rpm for 5 min and filtered by 0.4 μm filter paper with 100 mL of water for four times. Finally, all filtrates were collected and then diluted in a 1 L volumetric flask. Twenty milliliters of the above-prepared solution was diluted to 100 mL as the spinach sample for further analysis.

### 3. Results and discussion

#### 3.1. Construction and morphological characterisation of the PtNPs/GCE

Figure 1(a) represents the electrodeposition process of platinum nanoparticles on the GCE by CV, which displays a gradually increased reduction peak current around 0.02 V with the augment of scan cycles. This phenomenon can be attributed to enhanced conductivity of platinum nanoparticles deposited on the surface of GCE. Figure 1(b) displays the characteristic CV curve of the prepared PtNPs/GCE in perchloric acid solution. The voltammetric peaks ranging from \(-0.05\) to \(-0.25\) V are associated with hydrogen adsorption and desorption. An anodic peak (broad) at around 0.9 V and a cathodic peak at around 0.40 V are also observed, corresponding to the formation of platinum oxides and...
the reformation of Pt(0), respectively. It confirms that Pt nanoparticles have been formed on the GCE. Moreover, the active surface area of PtNPs/GCE was calculated as 0.57 cm\(^2\) based on the hydrogen adsorption-desorption method [20] (which is appropriately sevenfold larger than that of the bare Pt electrode used in this work). The surface morphology of the PtNPs on the GCE was characterised by SEM. As shown in Figure 1(c), the spherical-like PtNPs disperse uniformly on the electrode surface and the average diameter of spherical particles is around \(\sim 300\) nm. Elemental identification of this modified electrode by EDX shows obvious Pt peaks in the spectrum of Figure 1(d) (carbon peak is attributed to GCE) which confirms that Pt nanoparticles have been attached to the electrode surface.

### 3.2. Electrochemical behaviours of OA at bare Pt electrode and PtNPs/GCE

Figure 2 exhibits cyclic voltammograms in the presence of OA obtained at a bare Pt electrode (a), a bare GCE (b) and the PtNPs/GCE (c). A small unobvious oxidative peak demonstrates limited catalytic activity of the GCE (curve b). The anodic peak at around 0.8 V corresponds to the oxidation of OA and the cathodic peak at around 0.40 V is associated with the reduction of platinum oxide film (curves a and c). It can be readily discovered
that an increased oxidised current response was received on account of the large augment of active surface area of platinum at the PtNPs/GCE. Both bare Pt electrode and PtNPs/GCE represent less OA oxidation overpotential. And the reaction mechanism of OA at a Pt electrode surface can be assigned to two parallel paths,[16,21] either involving an absorbed Pt oxygen species (PtO$_{ads}$) presented in Equations (2) and (3) or referring to a direct electron transfer from OA absorbed at Pt surface (Eq. (4)).

\[
\begin{align*}
Pt + H_2O & \leftrightarrow PtO_{ads} + 2H^+ + 2e^- \\
H_2C_2O_4aq + PtO_{ads} & \rightarrow Pt + 2CO_2 + H_2O \\
H_2C_2O_4ads + Pt(II) & \rightarrow Pt + 2CO_2 + 2H^+
\end{align*}
\]

3.3. Effect of applied potential

To figure out the optimal detection sensitivity, the applied voltage was explored around the oxidation peak potential of OA from 0.75 to 1.05 V by amperometry. 0.1 M perchloric acid was selected as supporting electrolyte where the electrochemical oxidation activity of OA was higher than in sulphuric acid at pH < 2.5.[22] Figure 3(a) shows that the current

![Figure 2. CV curves obtained at a bare Pt electrode (a), a bare GCE (b) and PtNPs/GCE (c) in 0.1 M HClO$_4$ containing 2 mM of OA at a scan rate of 100 mV s$^{-1}$.](image)

![Figure 3. Amperometric response of bare Pt electrode (a) and PtNPs/GCE (b) with successive addition of 10 µL 2 mM OA under stirring in 0.1 M HClO$_4$ solution at different potentials.](image)
of oxidation enhances after successive addition of 10 μL 2 mM OA at different potentials with a bare platinum electrode. The response to OA increases with increase in the applied potential positive shift from 0.75 to 0.90 V. Nonetheless, when the voltage continues to increase from 0.95 V to 1.05 V, the sensitivity of current weakens as the adsorbed oxygen (or oxide) on the electrode surface prevents the adsorption and oxidation of OA at higher potentials. It is observed from Figure 3(b) that the amperometric response is increasing with the increment of applied potential from 0.75 to 0.95 V at the PtNPs/GCE, but the noise of response largely enhance at 1.05 V. Thus, the applied potentials of 0.9 V and 0.95 V were chosen to determine OA corresponding to the bare platinum electrode and PtNPs/GCE, because these potentials were more sufficient than the peak potential of 0.8 V to trigger OA to be fully oxidised at the required time scale. With regard to the different optimal applied potentials, it is most likely because PtNPs/GCE with higher sensitivity reveals wider oxidation range, as illustrated in Figure 2.

### 3.4. Amperometric response and calibration curve for OA detection

Figures 4(a) and (c) display the current responses obtained for sensing of OA at the bare Pt electrode and PtNPs/GCE at the potential of 0.9 V and 0.95 V, respectively. When the

![Figure 4](image-url)

**Figure 4.** Amperometric $i-t$ curves of bare Pt electrode (a) and PtNPs/GCE (C) with the addition of 2 mM OA into a homogeneously stirred 0.1 M HClO₄ every 50 seconds at 0.9 V and 0.95 V. (b) and (d) corresponding calibration curves of current versus OA concentrations for bare Pt electrode and PtNPs/GCE. Error bars are the standard error of the mean ($n = 5$ electrodes).
background current was gradually stabilised, 2 μL (Figure 4(a)) or 4 μL (Figure 4(c)) of 2 mM OA was added into 7 mL of 0.1 M HClO₄ solution every 50s intervals for 12 times with homogeneously stirring and the increased amperometric signal was due to OA oxidation. Afterwards, 40 μL (Figure 4(a)) or 100 μL (Figure 4(c)) of 2 mM OA was added for 26 times or 37 times. The linear calibration plots of current versus OA concentration were shown in Figure 4(b,d). It manifests good linear range for the bare Pt electrode containing segments: 0.57–104.01 μM (correlation coefficient \( R^2 = 0.99559 \)) with a sensitivity of 5.03 ± 0.1 μA/mM and 104.01–228.75 μM (correlation coefficient \( R^2 = 0.99183 \)) based on repeated measurements on different electrodes \( (n = 5) \). The PtNPs/GC electrodes \( (n = 5) \) present higher sensitivity of 17.89 ± 0.2 μA/mM in the range of 1.14–342.80 μM with a correlation coefficient \( R^2 = 0.99505 \) and 342.80–548.92 μM (correlation coefficient \( R^2 = 0.99299 \)). This higher sensitivity and wider detection range are due to the larger active area of PtNPs deposited on the GCE and these observations are in line with the expectation of tungsten carbide nanotubes (WC NTs) supported platinum nanoparticles, where WC substrate also shows efficient conductivity and provides rapid electron transport pathways.[18] The limit of detection of the bare Pt electrode was 0.38 μM by calculating from Figure 4(b) \( (S/N = 3, n = 5) \) based on Equation (1). The standard deviation of three repeated tests was less than 1.67%. The PtNPs/GC electrode possessed a comparable limit of detection of 0.28 μM \( (S/N = 3, n = 5) \) and the standard deviation was no more than 2.04%.

A detailed comparison of linear detection ranges and detection limits of different OA sensors has been summarised in Table 1. In contrast with the previously reported electrochemical sensors using different electrodes, the Pt electrode and PtNPs/GCE manifest relatively lower detection limits. In particular, they are suitable for the determination of OA at low concentrations. Moreover, another important issue should be addressed that there

| Electrode materials                                      | Linear range (μM) | Detection limit of OA (μM) | References |
|--------------------------------------------------------|-------------------|---------------------------|------------|
| Carbon nanotubes-modified electrode                     | 50–15,000         | 12                        | [14]       |
| Platinum nanoparticles modified on graphene nanosheets  | 100–15,000        | 10                        | [17]       |
| Tungsten carbide nanotubes supported platinum nanoparticles | 0–0.125          | 0.012                     | [18]       |
| TiO₂ nanoparticles/multiwalled carbon nanotubes modified electrode | 100–1000          | 33                        | [23]       |
| Graphene Aerogel                                       | 4–100             | 0.8                       | [24]       |
| Palladium nanoparticle loaded carbon nanofiber modified electrode | 200–13,000, 13,000–45,000 | 200               | [25]       |
| PdAu alloy nanoparticles on ionic liquid functionalised graphene film | 5–100             | 2.7                       | [26]       |
| Cobalt(II) phthalocyanine on a SiO₂/SnO₂ matrix surface | 50–1000           | 30                        | [27]       |
| Exfoliated graphite-polystyrene composite electrode     | 500–3000          | 50                        | [28]       |
| Multi-walled carbon nanotube-gold nanoparticle composite | 1–800             | 1                         | [29]       |
| Graphene-modified carbon ionic liquid electrode         | 8–6000            | 0.48                      | [30]       |
| Palladium-doped mesoporous silica SBA-15 modified in carbon-paste electrode | 0.57–104.01, 104.01–228.75 | 0.38            | This work |
| Bare platinum electrode                                 | 1.14–342.80       | 0.28                      | This work  |
| Platinum nanoparticles modified glassy carbon electrode  | 1.14–342.80       | 0.28                      | This work  |
is no complicated electrode preparation procedures required by our reported sensors. All these indicate that a bulk Pt electrode even without further decoration is a successful candidate for OA determination.

### 3.5. Reproducibility, stability and selectivity of the bare Pt electrode and PtNPs/GCE

The reproducibility of the both electrodes was investigated by six replicate measurements using CV. The relative standard deviations (RSDs) of the OA oxidation peak currents by six successive tests were 3.69% (Pt electrode) and 5.13% (PtNPs/GCE).

It is well known that stability is crucial premise for sensors in their practical application. The stability of sensors was evaluated by the same sensor for four repeated experiments. It was found that the current of OA oxidation decreased to 69.9% (Pt electrode) and 77.4% (PtNPs/GCE) of their initial values in 20 hours without activation as a result of the passivation of the electrode surface. Therefore, these electrodes were activated in sulphuric acid solution before a measurement obtained a satisfactory result again, which showed that OA oxidation currents were recovered to 95.8% (Pt electrode) and 94.3% (PtNPs/GCE) after first scanned for 40 hours. The oxidation peak current was retained at 94.4% and 90.8% at the bare Pt electrode by storing in air at room temperature for 5 days and 10 days, respectively. As for the PtNPs/GCE, the oxidation peak current of OA decreased by 6.7% and 11.8% under the same condition. All of results demonstrate that the sensors are highly stable and the performance can be easily recovered as Pt electrode cleaning is routine work required by electrochemical laboratories, these make them available for long term use.

In order to evaluate the selectivity of the Pt electrode and PtNPs/GCE for the determination of OA, the effects of different potentially interfering organic (formic acid, acetic acid, tartar acid, citric acid and glucose) and inorganic (e.g. K⁺, Na⁺, Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺ and Mn²⁺) substances were studied. Figure 5(a) illustrates amperometric response with the addition of 2 μL of 2 mM OA and a 100-fold excess of formic acid (a), acetic

![Figure 5](image_url)

**Figure 5.** Amperometric $i-t$ curve response of the bare Pt electrode (a) and the PtNPs/GCE (b) with the addition of 2 μL (bare Pt electrode) and 4 μL (PtNPs/GCE) of 2 mM OA and a 100-fold excess of interference compounds, for example, formic acid (a), acetic acid (b), tartar acid (c), citric acid (d), glucose (e), K⁺ (f), Na⁺ (g), Ca²⁺ (h), Mg²⁺ (i), Cu²⁺ (j), Zn²⁺ (k) and Mn²⁺ (l) into a homogeneously stirred system containing 0.1 M HClO₄ solution every 50 seconds at the potential of 0.9 V and 0.95 V.
acid (b), tartar acid (c), citric acid (d), glucose (e), K⁺ (f), Na⁺ (g), Ca²⁺ (h), Mg²⁺ (i), Cu²⁺ (j), Zn²⁺ (k) and Mn²⁺ (l) every 50 seconds in 0.1 M HClO₄ by bare Pt electrode with homogeneously stirring at the potential of 0.9 V. The above-mentioned test procedure was conducted for the PtNPs/GCE except using 4 μL of 2 mM OA at the potential of 0.95 V (Figure 5(b)). From Figure 5(a,b), the current value increased by stepwise addition of OA and yielded little current response followed by the further addition of different interferents every 50 seconds, indicating that the bare Pt electrode and the PtNPs/GCE have significantly high selectivity towards OA.

3.6. Real samples detection

Determination of OA level in food provides important basis for food quality monitoring and the diet of clinical patients. For the purpose of verifying the application of bare Pt electrode and PtNPs/GCE, they were applied to determine OA in a real spinach sample by amperometry (Figure 6(a,b)). 10 μL or 20 μL of prepared spinach samples was added in the test system and the current response was increased accordingly. Based on the linear response range shown in Figure 4(b,d), the content of OA can be measured. For comparison, the traditional standard potassium permanganate titration was also performed on the same sample. As indicated in Table 2, the content of OA in the real spinach samples was 10.61 mg g⁻¹ at bare Pt electrode, 10.49 mg g⁻¹ at PtNPs/GCE and 10.70 mg g⁻¹ by standard titration method with six repetitive experiments respectively, which were comparable to 9.70 mg g⁻¹ listing in the U.S.

| Detection method | Electrode materials | OA content in spinach samples (mg g⁻¹) | RSD (%), n = 6 |
|------------------|---------------------|----------------------------------------|----------------|
| Titration method | —                   | 10.70                                  | 4.49           |
| Amperometry      | Bare Pt electrode   | 10.61                                  | 3.90           |
|                  | PtNPs/GCE           | 10.49                                  | 3.62           |
Department of Agriculture,[5] indicating that both electrodes are efficient for the determination of OA in real vegetable samples.

4. Conclusions
In conclusion, the bare Pt electrode exhibits good linear OA detection ranges of 0.57–104.01 μM and 104.01–228.75 μM and a low detection limit of 0.38 μM (S/N = 3). Nevertheless, it is well known that bare electrode have demerit of low sensibility. By contrast, due to larger active surface area of PtNPs, the PtNPs/GCE proves enhanced sensibility with lower detection limit of 0.28 μM (S/N = 3) and wider linear concentration ranges of 1.14–342.80 μM and 342.80–584.92 μM. Both electrodes show good stability, reproducibility and can be further successfully employed for determining OA content of real spinach samples. Most importantly, the performance of Pt electrode is easy to be recovered for reuse by simply activated in sulphuric acid solution, which makes it quick and convenient to be applied in the promising clinical diagnosis and foodstuff analysis alone potentially.

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No potential conflict of interest was reported by the authors.

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