Electrocatalytic oxidation of formaldehyde and formic acid at Pd nanoparticles modified glassy carbon electrode

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Pd nanoparticle (NP) modified glassy carbon electrodes were prepared by the electrochemical deposition method of cyclic voltammetry (CV) and the potentiostatic technique, respectively. Scanning electron microscopy was used to characterise the morphology of the NP-modified electrode's surface. The electrocatalytic oxidation of formaldehyde and formic acid were investigated at the modified electrodes by CV and linear sweep voltammetry. The experimental results show that the electrodes display remarkable electrocatalytic activity and long-term stability for the oxidation of formaldehyde and formic acid. The oxidation mechanism of formaldehyde and formic acid on the modified electrodes is discussed primarily. The experimental parameters were optimised for establishing the methods of formaldehyde and formic acid determination. The oxidation peak current is linearly proportional to the concentration of formaldehyde in the range of 1.0×10^{-4}–1.4×10^{-2} M with the detection limit being 3.0×10^{-5} M and relative standard deviation (RSD) being 3.9%. The linear dynamic range of formic acid is in the range of 1.0×10^{-5}–1.0×10^{-2} M, the detection limit is 4.0×10^{-6} M and the RSD is 2.8%. The low detection limit, wide linear range and high sensitivity of the sensors make them valuable for further application.

1. Introduction: Currently, research into small organic molecule fuel cells is mainly focused on the preparation of efficient and stable catalysts. Moreover, the selection of suitable catalysts has long been the dominant direction in research on the electrochemical oxidation of small organic molecules [1–4] such as formaldehyde and formic acid. Like its sister metal Pt, Pd has a similar lattice structure, atomic radius and lattice energy, as well as high catalytic activity [5]. It is worth noting that Pd is a relatively inexpensive noble metal, so these are great further prospects for the development of Pd catalysts for the rapid catalytic oxidation of small organic molecules in the construction of electrochemical sensors and fuel cell applications. In a word, exploration of a simple chemical method to prepare a Pd catalyst has vital significance.

In recent years, Pd nanoparticles (NPs) have been prepared using different methods for the electrocatalytic oxidation of formic acid and formaldehyde [6–10]. For instance, Zhu *et al.* [11] reported the self-assembly of Pd NPs on functional multi-walled carbon nanotubes for formaldehyde oxidation. In previous researches, we have electrodeposited Pd NPs on a fullerene modified glassy carbon (GC) electrode for methane sensing [12]. In addition, a low-cost $Ni(OH)_2$/Ni electrode with simplicity of preparation was used for the electrocatalytic oxidation of formaldehyde and methanol [13]. In fact, many formaldehyde and formic acid detection methods are not sufficiently sensitive enough, or are time consuming, or use expensive instrumentations [6, 8]. In particular, to our knowledge, the electrochemical deposition of NPs towards the electrocatalytic oxidation of formic acid and formaldehyde, as well as to facilitate detection, have not been reported hitherto.

In the work reported in this Letter, GC electrodes modified with Pd NPs were prepared using different electrodepositing methods, and the electrocatalytic behaviour of the modified electrodes towards the oxidation of formic acid and formaldehyde were studied by cyclic voltammetry (CV). By optimising the experimental conditions, improved electrocatalytic activity for the formic acid and formaldehyde oxidation was achieved, and the oxidation mechanism is discussed using linear voltammetry. In addition, facile electrochemical methods for the determination of formaldehyde and formic acid were established.

2. Experimental

2.1. Apparatus and reagents: All the electrochemical analyses were performed on a CHI660 electrochemical analyser (Chenhua, Shanghai, China). A three-electrode cell with a GC working electrode, Pt wire as the auxiliary electrode and Ag/AgCl as the reference electrode, was employed. All solutions were prepared with ultrawater (Millipore Milli-Q water, 18 MΩ cm) and purged with N_2 gas before and during each experiment. SEM measurements were performed using a JEOL JSM-6700F instrument. The concentration of formaldehyde and formic acid solution was calibrated by the iodometric method [14].

2.2. Electrode modification: The GC electrode was polished successively with 1.0, 0.3 and 0.05 μm alumina powders on microcloth and then thoroughly cleaned ultrasonically with ethanol and doubly distilled water. The reference electrode was washed with doubly distilled water. The auxiliary electrode was ultrasonically cleaned with diluted HNO_3 and then burned for 2 min to remove organic compounds adsorbed on the electrode.

The treated GC electrode was immersed in 1.5×10^{-3} M $PdCl_2$–HCl solution and CV scans (−0.4–0.8 V) at a scan rate of 25 mV/s were applied to the electrode. After 15 cycles, the Pd NPs were deposited on the surface of the GC electrode and a Pd/GC/CV electrode was obtained. For the Pd/GC electrode, the deposition of NPs was performed at a constant potential of −0.9 V for 25 min [15]. The prepared electrodes were washed and soaked in distilled water before use. All the experiments were conducted at room temperature.

3. Results and discussion

3.1. Characterisation of electrode: Fig. 1 shows the CVs of Pd deposition on the GC electrode. The peaks at 0.60 V in the forward potential scan correspond to the Pd ion dissociation. The peaks at 0.01 V (first cycle) and 0.12 V (second and third cycles) in the negative potential scan correspond to the reduction of Pd ion to Pd NPs, which are deposited on the surface of the GC electrode. The reduction potential of the Pd ion was found to shift positively from 0.01 V in the first cycle to 0.12 V in the second and third cycles, which is because the nucleation effect of Pd NPs on GC occurs only in the first cycle [16].

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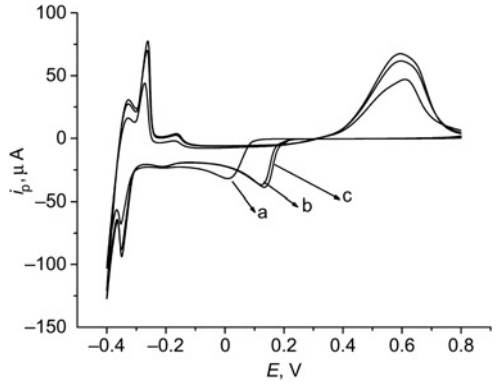


Figure 1 *CVs of Pd deposition on GC electrode in a solution of 1.5 × 10^{-3} M $PdCl_2$–HCl, (a) the first scan, (b) the second scan, (c) the third scan; scan rate: 25 mV/s*

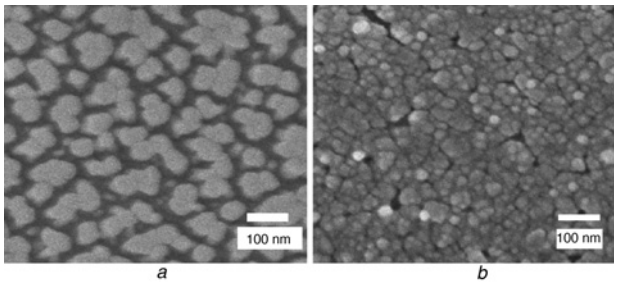


Figure 2 *SEM image of Pd NPs electrodeposited at Pd/GC/CV electrode by CV method and Pd/GC electrode by potentiostatic method*
a Pd/GC/CV electrode by CV method
b Pd/GC electrode by potentiostatic method

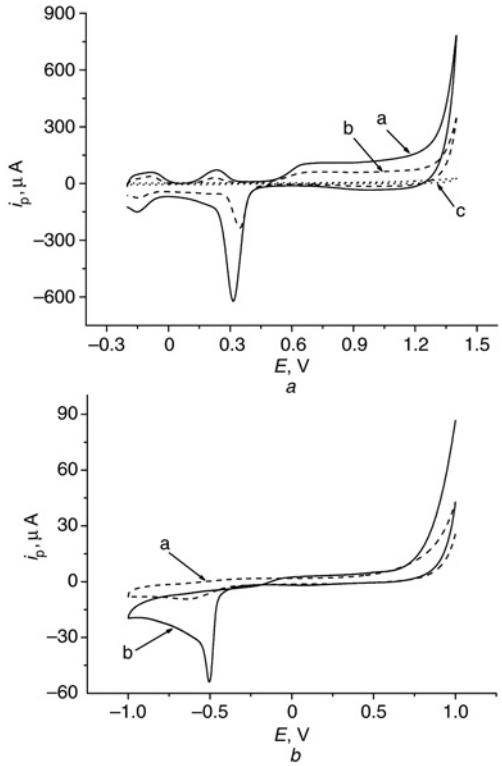


Figure 3 *Fig. 3a: CVs of Pd/GC electrode (a), Pd/GC/CV electrode (b) and GC electrode (c) in 0.5 M H_2SO_4; scan rate: 100 mV/s. Fig. 3b: CVs of Pd/GC electrode (a) and Pd/GC/CV electrode (b) in 0.1 M NaOH; scan rate: 100 mV/s*

The surface morphologies of the Pd/GC and Pd/GC/CV electrodes were characterised by SEM and the corresponding results are shown in Figs. 2*a* and *b*, respectively. The SEM images show that the Pd NPs are uniformly dispersed on the electrode's surface. Based on the SEM analysis, the electrodeposited Pd NPs have been found to be in the size range of 100–200 nm for Pd/GC/CV and 20–40 nm for Pd/GC, respectively. Moreover, the SEM analysis results authenticate the deposition of Pd NPs on the electrode's surface.

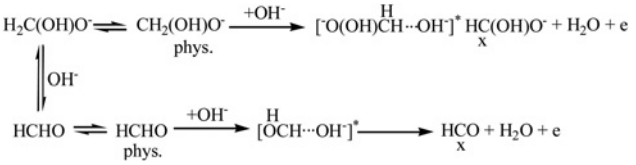
Fig. 3*a* shows the CVs of the Pd/GC, Pd/GC/CV and GC electrode's in 0.5 M H_2SO_4 electrolyte solution. The curves a and b have the same basic shape, where the peak current for the Pd/GC electrode is higher than for the Pd/GC/CV. This may be attributed to the fact that the Pd NPs prepared by the potentiostatic method have smaller particles size and larger surface area than those by the CV method. It can be seen from Fig. 3*a* that the Pd/GC electrode exhibits peaks at around −0.09 and 0.23 V corresponding to the adsorption/desorption of hydrogen, respectively. The formation of PdO and PdO_2 is in the potential region above 0.6 V, and the CV curve in the potential region from 1.4 to 0.9 V corresponds to the reduction of PdO_2. Moreover, the peak at 0.315 V corresponds to the reduction of PdO to Pd NP.

On the other hand, the CVs of the Pd/GC and the Pd/GC/CV electrode in 0.1 M NaOH are shown in Fig. 3*b*. The sharp reduction peak at −0.50 V in curve b corresponds to the reduction of Pd oxide, indicating that the Pd NPs have been immobilised on the surface of the GC electrode. In curve b of Fig. 3*b*, the ill-defined peak at about 0.00 V should be attributed to the formation of Pd $(OH)_2$ or PdO. The peak at a potential higher than 0.60 V corresponds to the formation of high valence Pd compounds, such as PdO_2 and PdO_3 etc. It was found that the redox peak in the curves for Pd/GC is lower than that of Pd/GC/CV, which may be because of a certain degree of agglomeration of Pd NPs arising from the smaller particle size and higher surface energy of the former in the alkaline medium. In the meantime, the GC electrode displays a poor response in both the acidic and the alkaline medium.

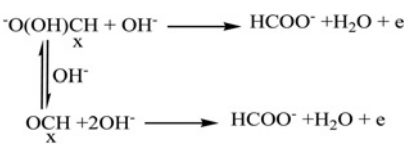
3.2. Electrocatalytic oxidation of formaldehyde: The electrocatalytic oxidation of formaldehyde was investigated by CV using the Pd/GC/CV and the GC electrode as the working electrode, respectively. No obvious redox peaks were observed for the GC electrode, suggesting that formaldehyde is inactive at the GC electrode. In Fig. 4, the Pd/GC/CV electrode shows oxidation peak I at −0.06 V in the positive potential scan and peak II at −0.48 V in the reverse scan. It is observed that the currents of formaldehyde oxidation peaks I and II are considerably high, indicating that the deposited Pd NPs have excellent electron transport properties as well as better electrocatalytic activity towards the oxidation of formaldehyde. Moreover, no apparent reduction peak was observed in the CVs, indicating that the oxidation of the formaldehyde at the Pd/GC/CV electrode is completely irreversible.

As stated by Betowska-Brzezinska and coworkers [17], the oxidation of formaldehyde is carried out in the following two steps:

The first step



The second step



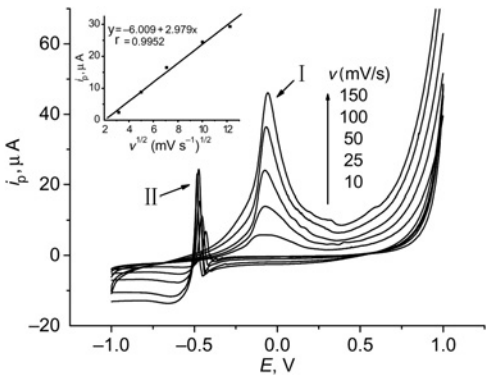


Figure 4 *CVs of Pd/GC/CV electrode in the solution of 8.0×10^{-3} M HCHO + 0.1 M NaOH at various scan rates of 10–150 mV/s*
Inset: Linear plot of peak current (I) and the square root of the scan rate in this condition

In the alkaline medium, geminal diol is generated in the electro-oxidation of formaldehyde, which is an electrically active material in the oxidation of various aldehydes. According to the literature, formic acid is the main product in the electrocatalytic oxidation of formaldehyde [18]. It can be concluded that oxidation peak I corresponds to the first step, and oxidation peak II corresponds to the second step [19]. Furthermore, the CV behaviour of the Pd/GC/CV electrode was investigated at various scan rates. As shown in Fig. 4, the oxidation peak currents of formaldehyde increase with increasing scan rate, and a good linear relationship is found between the peak current and the square root of the scan rate in the range of 10–150 mV/s, with a correlation coefficient of 0.9952. Therefore the oxidation of formaldehyde on the Pd/GC/CV electrode is a diffusion-controlled process.

3.3. Analytical features and application: After optimisation of the experimental conditions, 15 CV scans and 0.1 M NaOH solution were applied on the basis of sensitivity for formaldehyde determination. A linear relationship is obtained between the concentration of formaldehyde and the oxidation peak current in the range of 3.0×10^{-5}–1.4×10^{-2} M, and corresponds to the following equation: $i_p/\mu A = 4.060 \times 10^{-3} + 2.970c/M$, ($r = 0.9960$); the detection limit is 1.0×10^{-5} M.

The parallel determination of an 8.0×10^{-3} M formaldehyde solution was performed six times using the same one Pd/GC/CV electrode, and the relative standard deviation of the peak current is 3.9%, indicating good reproducibility of the electrode. The selectivity experiments suggest that 1000-fold concentration of Na^+, K^+, Cl^-, SO_4^{2-}, NO_3^-, a 100-fold concentration of NH_4^+ and a fivefold concentration of methanol, ethanol and acetone do not interfere with the formaldehyde determination. After the modified electrode was cleaned and stored at 4°C for 30 days, the value of the response current was still maintained at more than 80% of the initial, which shows good long-term stability of the Pd/GC/CV electrode. In the selected experimental conditions, recovery experiments were performed by the standard-addition technique using the Pd/GC/CV electrode as a working electrode. The recovery percentage values range between 94.7 and 104.0%.

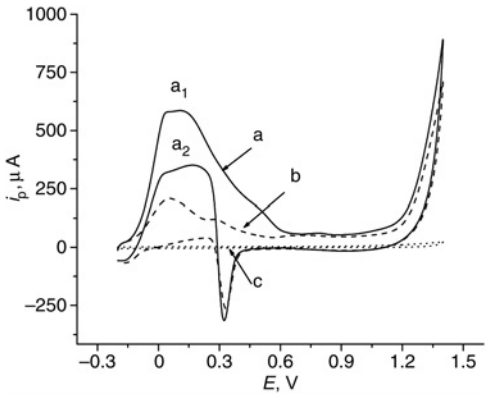


Figure 5 *CVs of the Pd/GC electrode (a), Pd/GC/CV electrode (b) and GC electrode (c) in a solution of 0.1 M H_2SO_4 + 0.01 M HCOOH; scan rate: 100 mV/s*

3.4. Electrocatalytic oxidation of formic acid: Fig. 5 shows the CV of electrocatalytic oxidation of formic acid on the Pd/GC electrode, Pd/GC/CV electrode and GC electrode, respectively. No obvious redox peak can be observed in curve c of Fig. 5, which shows that formic acid is inactive at the GC electrode. The catalytic oxidation of formic acid at the Pd/GC electrode exhibits a similar peak shape to the Pd/GC/CV electrode, but the peak current for the Pd/GC electrode is about three times as much as the Pd/GC/CV electrode. The Pd/GC electrode displays much higher electrocatalytic activity in the electro-oxidation of formic acid than the Pd/GC/CV electrode, which is attributed to the smaller catalyst particle size, larger surface area and more active sites at the Pd/GC electrode.

In Fig. 5, the oxidation peak a_1 at 0.103 V in the positive scan and the oxidation peak a_2 at 0.12 V in the negative scan with high peak current are apparent. Obviously, this suggests that the deposited Pd NPs have excellent electron transport properties and better electrocatalytic activity towards the oxidation of formic acid.

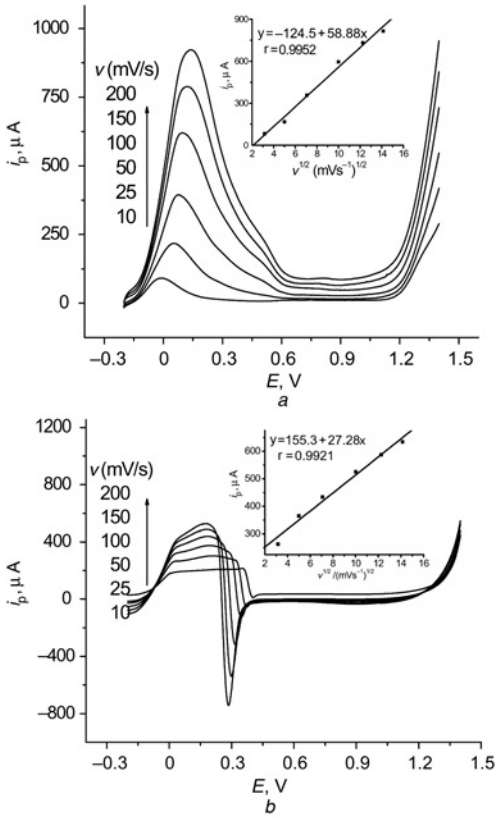


Figure 6 *Linear sweep voltammogram of the Pd/GC electrode in a solution of 0.1 M H_2SO_4 + 0.01 M HCOOH at various scan rates of 10–200 mV/s*
a Oxidation peak a_1 (in positive scan from −0.2 to 1.4 V)
b Oxidation peak a_2 (in negative scan from 1.4 to −0.2 V)
Inset: Linear plot of oxidation peak current and the square root of the scan rate

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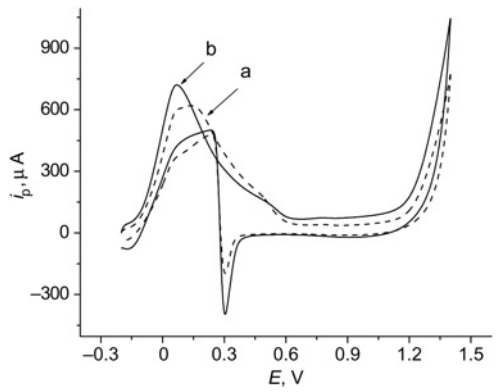

Figure 7 *CVs of the Pd/GC electrode in 0.01 M HCOOH in the absence (a) and presence (b) of Pd^{2+}; scan rate: 100 mV/s*

Figs. 6*a* and *b* are the segment display of the linear sweep voltammogram of the Pd/GC electrode at various scan rates. They show that in the electro-oxidation of formic acid on the Pd/GC electrode, the current of oxidation peaks a_1 and a_2 all increase with the increase of scanning rates, and they are proportional to the square root of the potential scanning rates, with correlation coefficients of 0.9952 and 0.9921, respectively. It is concluded that the oxidation of formic acid on the Pd/GC electrode is mainly controlled by the diffusion process.

According to the Laviron equation [20, 21]

$$E_p = \frac{RT}{\alpha nF}\ln\frac{RTK^0}{\alpha nFv}$$

The plot of E_p to lnv, a linear regression equation was as follows: $E_p = 0.3902 + 0.01685\ln v$, $R = 0.9907$. Thus, we derived $\alpha n = 0.9812$. Generally, α is assumed to be 0.5 in an irreversible electrode process. Hence, the number of electrons transferred of formic acid in the Pd/GC electrode is calculated approximately to be 2, which is consistent with the reported values [10, 22, 23]. The formic acid reaction equation presumably is

$$\mathrm{HCOOH_{ads(Pd)} \rightarrow CO_2 + 2H^+ + 2e^-}$$

Pavese and Solis [10] once pointed out that the binding interactions between Pd^{2+} and adsorbed species improve the activity of the electrode. To evaluate the role of Pd^{2+} in the reaction, $PdCl_2$ solution was added in the original experimental solution, and the results are shown in Fig. 7. The formic acid oxidation peak is significantly increased with the addition of $PdCl_2$, which confirms the role of Pd^{2+} in the surface activation of electrocatalysis at Pd/GC electrodes [24].

3.5. Analytical features and application: After optimisation of the experimental conditions, the constant potential of −0.9 V and the deposition time of 25 min were selected in the electrochemical deposition of Pd NPs for formic acid determination. A linear relationship is obtained between the concentration of formic acid and the oxidation peak current in the range of 1.0×10^{-5}–1.0×10^{-2} M, and corresponds to the following equation: $i_p/\mu A = 5.260 \times 10^{-1} + 7.530c/\mathrm{M}$, ($r = 0.9980$); the detection limit is 4.0×10^{-6} M and the RSD is 2.8%. The selectivity, long-term stability and reproducibility of Pd/GC are examined similar to Pd/GC/CV with satisfactory results.

4. Conclusions: Pd NPs were modified on the surface of the GC electrode by constant potential electrodeposition as well as the CV method, respectively. Electrocatalysis of formaldehyde and formic acid were performed using the modified electrodes. It was proved that the Pd/GC/CV and the Pd/GC electrodes have good electrocatalytic oxidation activity for formaldehyde and formic acid, and a possible oxidation mechanism of formaldehyde and formic acid is proposed. On this basis, new simple and low cost methods for the determination of formaldehyde and formic acid are established. With good stability and reproducibility, the newly developed methods have potential applications in the rapid detection of formaldehyde and formic acid, and the sensors studied in the present work are promising for use in fuel cells.

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6 References

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