Electrochemical degradation of formaldehyde with a novel Pd/GO modified graphite electrode

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A novel Pd/GO modified graphite electrode for anodic degradation of formaldehyde was successfully prepared via impregnation and electrodeposition processes. The surface morphology of the modified electrode was characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopic (XPS) techniques. The electrocalytic behavior of the electrode was characterized by cyclic voltammetry, it indicated that the modified graphite had excellent catalytic performance. The as-deposited Pd/GO/graphite modified electrode was applied to electro-degradation formaldehyde. Various factors influencing the degradation efficiency of formaldehyde such as current density, initial concentration of formaldehyde and initial pH were systematically investigated. The removal efficiency of formaldehyde, COD and TOC could reach 90.6%, 83.6% and 85% in pH 4 after 120 min electrolysis with a 0.5 mol L^{-1} Na_2SO_4 at a current density of 15 mA cm^{-2}, which gave the direct evidence of the electrocatalytic capability of the electrode. The electrochemical degradation of formaldehyde at Pd/GO/graphite followed pseudo-first-order kinetics. These results indicated that the Pd/GO/graphite modified electrode would be a promising anode for electrochemical degradation of formaldehyde.

1. INTRODUCTION

Formaldehyde is an important chemical widely used in many industries to manufacture building materials and house hold products [1–6]. However it is a major indoor chemical pollutant and is well recognized to be carcinogenic substance. The emission of formaldehyde can cause serious damage to the environment and humans. Thus the remove of formaldehyde has drawn extensive

attentions. At present, various methods of formaldehyde removal have been used by biological treatment [7], adsorption [8, 9], photocatalytic [10-12], plasma [13, 14], and thermal catalytic oxidation [15], yet there exist many limitations [16, 17]. The adsorption technology is limited by the adsorbent capacity, and the photocatalytic oxidation is easy to produce secondary pollution as well as having not efficient processing capacity. Plasma technique needs high cost. Thermal catalytic oxidation needs high temperature and high pressure. Therefore, an effective and low-cost method to formaldehyde removal needs to be developed.

Electrochemical degradation of organic pollutants has been investigated by many researchers [22-24]. And it has been proved as a cost-effective technology. Thus electrochemical degradation is a good choice of removing formaldehyde. As a new and attractive technology, electrochemical oxidation of organic pollutants has gained significant attentions over the past two decades [18-21]. The electrocatalytic degradation could resolve the possible secondary pollution due to the photocatalytic oxidation. One of the most important parts of electro-catalytic oxidation is obviously the electrode materials [27]. Good electrode materials should not only be effective in pollution degradation, but also be electrochemically stable and inexpensive.

There are many reports published about various modified electrodes materials. Safavi et al. [25] have developed palladium nanoparticles electrodeposited on carbon ionic liquid composite electrode for using electrocatalytic oxidation of formaldehyde. Ojani et al. [26] have investigated palladium nanoparticles on TiO_2 nanotube electrode to be applied to electrochemical oxidation of formaldehyde. Considering the graphite electrodes's (GEs) advantages such as commercial availability, low costs and easy of modification [28-30], as well as the Pd/GO composite's excellent catalytic activity for small organic molecules [31-33], a novel Pd/GO/graphite modified electrode as the anode for electro-degradation of formaldehyde. The electrode was characterized by SEM, EDX, XRD, XPS and cyclic voltammetric. And the electrochemical degradation of formaldehyde in aqueous solution was studied by galvanostatic electrolysis using the modified electrode as anode under different conditions. In addition, the degradation of higher concentration formaldehyde was also investigated.

2. EXPERIMENTAL

2.1. Reagents and Materials

Formaldehyde, palladium chloride, concentrated sulfuric acid and other reagents are of analytical reagent grade. All solutions were prepared with double distilled water. Supporting electrolyte used in the cyclic voltammetry was 0.1mol L^{-1} NaOH and 0.5mol L^{-1} Na_2SO_4 in the degradation test.

2.2. Apparatus

The surface morphology of the electrode was analyzed with energy dispersive X-ray spectroscopy which was connected to a scanning electron microscope S4800 from Hitachi High-

Technologies Corporation, Japan. X-ray diffraction analysis was carried out using a D/Max-3C diffractometer (Japan) with Cu Kα radiation source (λ=0.15418nm). Cyclic voltammetry were performed on a CHI 660D electrochemical workstation (CH Instrumental Co. China) using a single-compartment cell with a conventional three electrodes. The modified electrode (d=6mm) was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrode, respectively.

2.3 Preparation of the Pd/GO/GE

Prior to experiment, the surface pretreatment of GE was performed by hand polishing of the electrode surface with successive grades of emery papers down to 3000 grit up to a mirror finish. The polished electrode was then degreased with 1:1 nitric acid solution, acetone and washed with running doubly distilled water and utilized for further electrodeposition. GO/Pd composite was fabricated on the GE surface by a simple two-step process. 10μl of 1 mg mL^{-1} GO suspension was drop casted on the pre-cleaned GE and allowed to dry for 12 h at room temperature. Then the palladium nanoparticles electrodeposition was performed by cyclic voltammetry in a solution containing 1 mmol L^{-1} PdCl$_2$ and 0.1 mol L^{-1} hydrochloric acid. In which twenty consecutive cyclic voltammograms were recorded in the sweeping potential range between 0.4 to -0.25V and the scan rate was set at 50 mV s^{-1} [32]. The loading of Pd on the GO/GE surface was determined by inductively coupled plasma (ICP). For comparison, Pd/GE electrode was also prepared by electrodeposition of Pd on the surface of graphite under the same experimental conditions.

2.4 Formaldehyde degradation

The electrochemical degradation experiments were carried out by batch processes and the apparatus mainly consisted of a DC power supply, a heat-gathering style magnetic stirrer and a glass reactor. The anode was the modified electrode and cathode was stainless steel mesh surrounding the anode. The distance of the anode and cathode was 2 cm. For electrochemical degradation of formaldehyde tests, electrochemical cell with 100mL of 0.05mol L^{-1} formaldehyde solution and 0.5 mol L^{-1} Na$_2$SO$_4$ as supporting electrolyte were used. The experiments were conducted with different constant applied current density, with constant current used, and stainless steel cathode and magnetic stirrer was used for solution mixing.

High Performance Liquid Chromatography (HPLC) with an ultraviolet detector of 355 nm wavelength and a Supelco LC-18 column was used to monitor the changes of the formaldehyde concentration during the course of electrochemical oxidation. The mobile phase was composed of 35% ultrapure water/65% acetonitrile. Isocratic elution at a flow of 1.0 mL/min^{-1}. Values of total organic carbon (TOC) were measured with a Shimadzu TOC-VCPH analyzer. Potassium dichromate method was used to evaluate chemical oxygen demand (COD).

3. RESULTS AND DISCUSSION

3.1. Characterization

Fig. 1(A-E) showed the SEM images of the surface morphology of GO/GE, Pd/GE, Pd/GO/GE. Fig. 1(A) and (B) showed SEM images of Pd/GE with different magnification. It can be seen that Pd nanoparticles are deposited on graphite surface, however, their dispersion is not uniform and some Pd nanoparticles agglomerated together. The conglobatus Pd nanoparticles easily dropped from GE surface, which will result in shorter electrode durability, lower conversion efficiency and secondary pollution of Pd nanoparticles. Fig. 1(C) showed the surface of GO/GE, GO layers with plenty of wrinkles owing to the thin structure of the sheet could found on the electrode surface. Compared with Pd/GE (Fig. 1(A) and 1(B)), the Pd/GO/GE composite electrode displays a more uniform and compact morphology (Fig. 1(D) and 1(E)). And the deposited Pd particles in the presence of GO are obviously smaller, and have sufficient number of active catalytic sites and large surface area. Furthermore, the EDS spectrum of the Pd/GO/GE (Fig. 1(F)) confirms the presence of Pd.
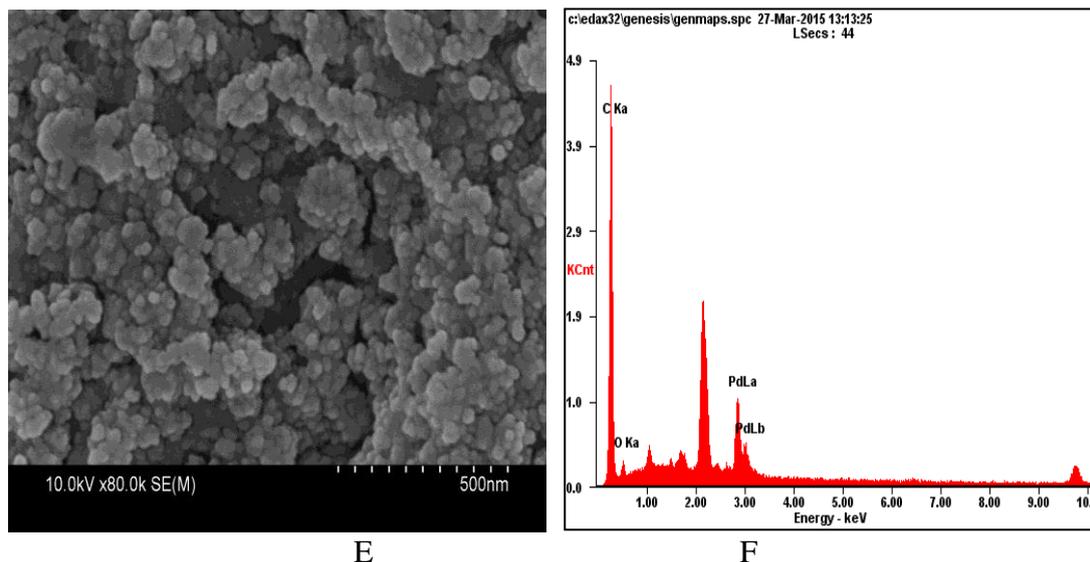

A

B

C

D
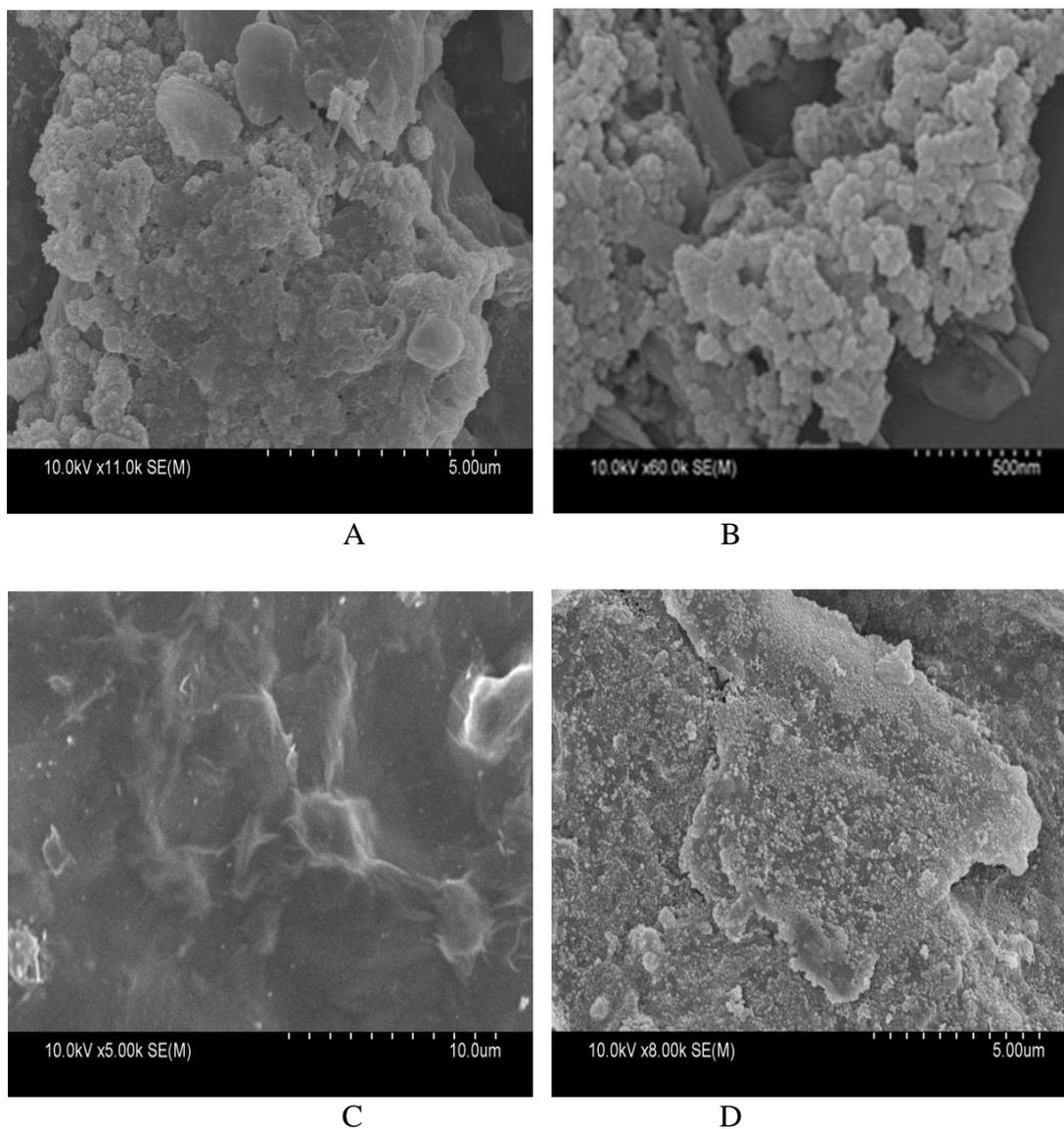
Figure 1. The SEM images of Pd/GE (A), GO/GE (C), Pd/GO/GE (D), higher magnification SEM images of Pd/GE (B), Pd/GO/GE (E), and EDS analysis of Pd/GO/GE (F).

Fig. 2 showed the XRD patterns of graphite and Pd/GO/GE electrodes. For the spectrum of graphite, the diffraction peak centered at 2θ of 26.5° is attributed to the (002) plane reflection of hexagonal crystalline graphite [36]. For the spectrum of Pd/GO/GE, it exhibits diffraction peaks at 2θ values of 10.94◦, 40.1◦and 46.6◦ corresponding respectively to the (001) and (111) planes of GO and Pd [37], confirming that Pd particles are successfully deposited on graphite electrode. This result was consistent with the SEM observation.
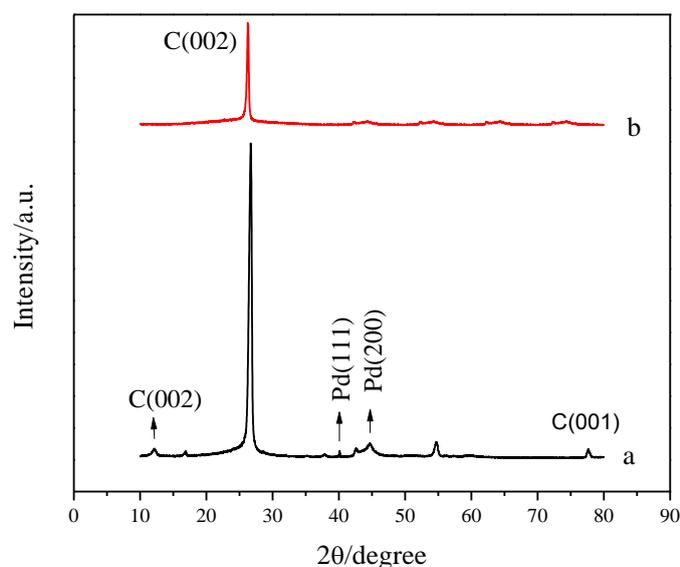

Figure 2. The XRD pattern of GO (a), Pd/GO/GE (b).

To further probe the content and chemical composition of the Pd/GO/GE, XPS measurements

were performed. In Fig. 3 (A), it can be seen that there is a peak near 340 eV corresponding Pd 3d, this indicated that the Pd nanoparticles deposited on the electrode successfully. Fig. 3 (B) presents the C 1s spectra of Pd/GO/GE, the main peak centered at 284.6 eV is associated with C-C bonds. Another peak centered at 286.6 eV is due to C-O bonds. It is due to the existence of oxygen-containing functional groups or hydroxyl, but it is weak obviously. Fig. 3(C) showed apparent Pd 3d signals of Pd/GO/GE. It can be deconvoluted into double peaks (335.5 eV and 341.1 eV) corresponding to metallic Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. From the XPS results, it can be concluded that the GO and Pd nanaoparticles can deposited on the electrode surface.
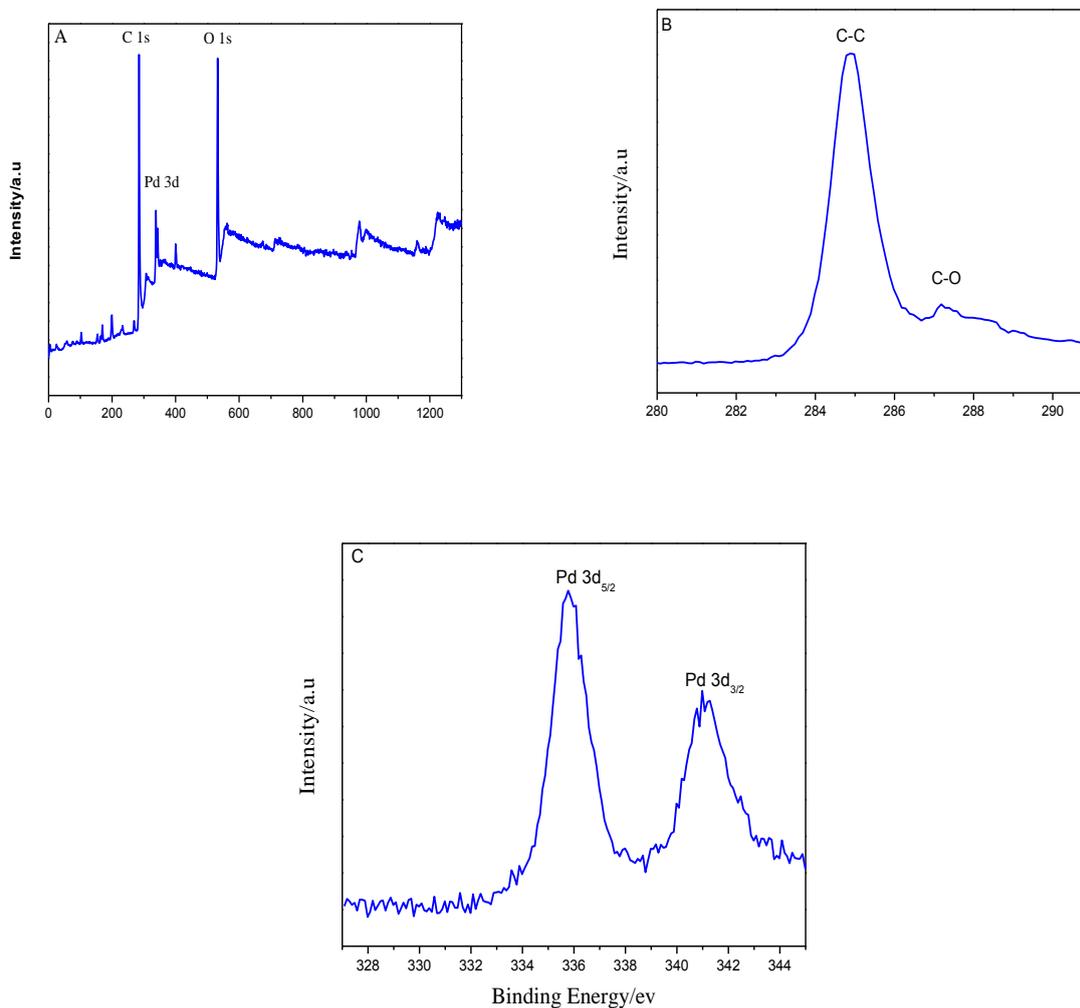

Figure 3. XPS spectra of Pd/GO/GE (A), C 1s XPS spectra of Pd/GO/GE (B), and the Pd 3d XPS spectra of Pd/GO/GE (C).

3.2. Cyclic voltammetry analysis

The electrooxidation of formaldehyde at the surfaces of Pd/GE and Pd/GO/GE composite electrode was investigated in 0.1mol/L^{-1} NaOH solution by cyclic voltammetry. At the beginning, the prepared electrode was dipped into the electrolyte, ten consecutive cyclic voltammograms were recorded in the potential range between -1.4 V to 1 V versus SCE at the scan rate of 50 mV s^{-1} to

obtain stable voltammogram. Then typical results obtained for a potential scan from -0.8 to 0.8 V versus SCE are shown in Fig. 4(a) and (b), respectively. As can be seen, two anodic peaks can be clearly observed in the cyclic voltammograms. The forward scan of the CV curves is characterized by a strong current peak mainly attributed to the oxidation of CO_{ads} to CO_2, resulted from dissociative adsorption of formaldehyde [35]. With the sweeping potential towards more positive values, COads was released from the surface and forward anodic peak was followed by a current drop due to the formation of Pd oxide layer which is nearly inactive for formaldehyde oxidation. In the reverse sweep, another anodic peak is observed due to the complete oxidation of HCHO to CO_2 via a dehydrogenation reaction [36].

The anodic peak current density reflects the amount of formaldehyde oxidized at the Pd electrocatalysts, and the anodic peak potential represents the ability of electrocatalysts to catalyze formaldehyde oxidation. Therefore, the anodic peak current density and the peak potential are two important parameters to evaluate the electrocatalytic activity of catalysts [37-39]. In comparison with (a) and (b), it can be observed that there is an increment in the peak current density and a decrease in oxidation onset potential and peak potential. The oxidation peak current density was 17.2 mA cm^{-2} at +0.14 V on the Pd/GE and 26 mA cm^{-2} at -0.02 V on the Pd/GO/GE. These data can be attributed to that the large electrochemical active surface area of the electrodes due to that graphite as a carbon based support has a good adhering strength for nanoparticles. The higher electrocatalytic activity of the Pd/GO/GE may be related to that the thinnest 2D structure of graphene oxide can prevent metal nanoparticles from agglomerating in turn. On that account, graphene oxide sheets enhance the surface area of the nanocatalyst supported by them effectively, which eventually leads to a rise in catalytic activities [31, 40, 41]. In this section, a comparative study was done for the present electrode and some previous works in terms of onset and peak potential of formaldehyde oxidation (Table 1). From the data, it is evidence that the Pd/GO/GE has superb performance and can it act as an active electrode for formaldehyde oxidation.
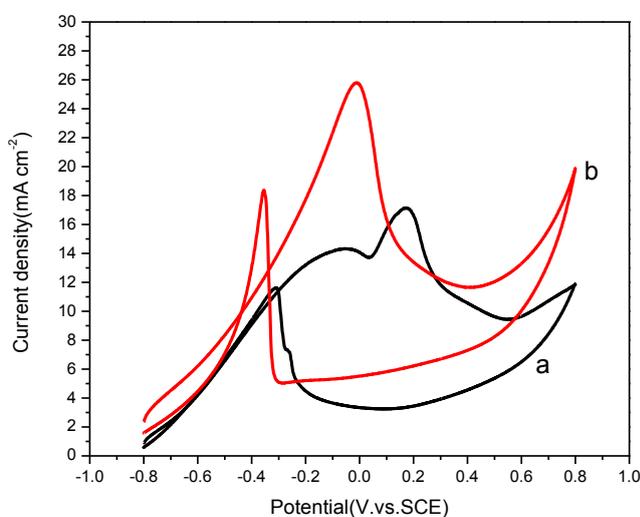

Figure 4. CVs of 0.03mol L^{-1} formaldehyde in 0.1 mol L^{-1} NaOH solution at Pd modified electrode (a) and Pd/GO/GE modified electrode (b). Scan rate: 50 mV s^{-1}.

Table 1. Comparison of the efficiency of Pd/GO/GE with some of the previously reported electrodes for formaldehyde oxidation.

Modified electrode	$C_{Electrolyte}/C_{Formaldehyde}$ (M)	V(mV s^{-1})	$E_p$vs.SCE/V	j(mAcm^{-2})	References
Pd–fMWNT	0.1 mol/L NaOH 0.3	50	0.7	82	(35)
Pt–Pd/SWCNT	0.5 mol/L H$_2$SO$_4$ 0.5	50	0.78	33.56	(48)
Pd–CILE	0.1 mol/L NaOH 0.3	100	0.15	9.8	(24)
Pd-MWNT/GCE	0.1 mol/L NaOH 0.3	50	0.42	9.7	(43)
Pt/PAANI/MWNTs/GCE	0.5 mol/L H$_2$SO$_4$ 0.5	50	0.45	7.32	(44)
Pt/PAANI/GCE	0.5 mol/L H$_2$SO$_4$ 0.5	50	0.50	5.63	(44)
Cu/P(2ADPA)/MCNTPE	0.1 mol/L NaOH 0.17	20	0.63	24.56	(45)
Pd/TiO$_2$NT/Ti	0.1 mol/L NaOH 0.051	100	0.01	20.4	(25)
Pd/GE	0.1 mol/L NaOH 0.03	50	0.14	17.2	This work
Pd/GO/GE	0.1 mol/L NaOH 0.03	50	-0.02	26	This work

3.3. Effect of formaldehyde concentration and scan rate

Fig. 5 shows the cyclic voltammetric response of Pd/GO/GE electrode in the presence of different concentrations of formaldehyde. It can be seen that both forward and backward oxidation peak potentials shifted towards more positive values and the peak current density increased with adding formaldehyde concentration. Moreover, increase in the concerntration of formaldehyde caused an increase in anodic currents. We assume that this effect caused by saturation of active sites at the surface of electrode and also contamination of the catalyst surface which is mainly arisen from the COads intermediate during the formaldehyde oxidation. CVs of 0.03M HCHO in 0.1M NaOH solution at Pd/GO/GE with different scan rates is shown in Fig. 6. The result reveals that as the scan rate increased, the forward oxidation peak currents increased and their peak potentials shifted slightly towards positive directions. In the case of backward anodic peak, increase in the sweeping rate can cause the peak potential to shift negatively while peak currents remained nearly constant. The current of the forward scan peak was linearly proportional to the square root of scan rate within some range, which indicates that oxidation may be controlled by a diffusion process in a range of scan rates [51].
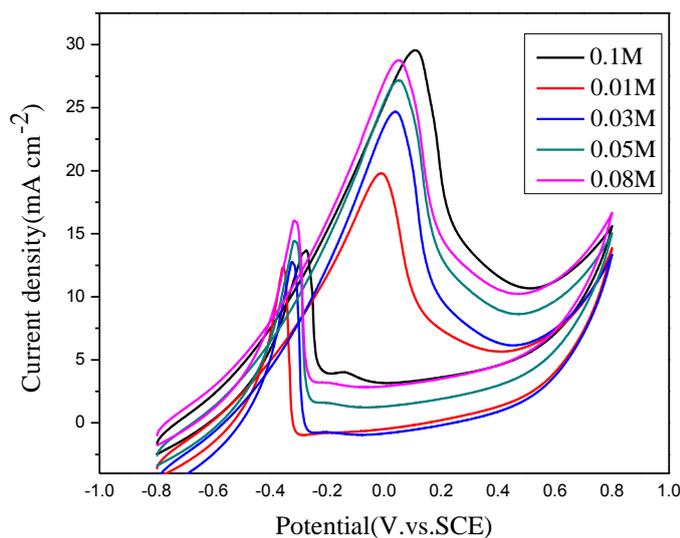
Figure 5. Cyclic voltammograms of different concentrations of formaldehyde in 0.1 M NaOH, (a-f: 0.010, 0.030, 0.050, 0.080, 0.10mol L^{-1}, at scan rate 50 mV s^{-1}).
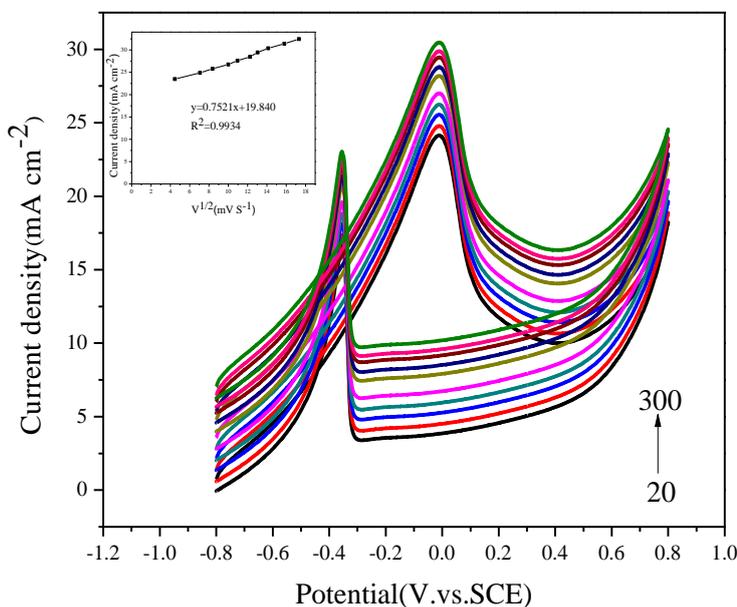

Figure 6. Cyclic voltammograms of 0.03mol L^{-1} HCHO in 0.1mol L^{-1} NaOH solution at the Pd/GO/GE at different scan rate: 20, 50, 70, 100, 120, 150, 170, 200, 250, 300mV s^{-1}. Insert: variation of forward anodic peak current density of HCHO versus $v^{1/2}$.

3.4. Electrocatalytic of formaldehyde using Pd/GO/GE electrode

3.4.1. Effect of different current density

A palladium nanoparticles and graphene oxide loading on graphite rod with a working area 2.5 cm^2 as an anode and a stainless steel wire surrounding the graphite rod with a distance of 2 cm as a

cathode were connected by a DC regulated power supply to constitute for the formaldehyde treatment. The current density was obtained in accordance with the current divided by the area of the anode. The initial concentration of formaldehyde during the experiment runs was 150 mg L^{-1} of a volume of 100mL, and Na_2SO_4 was used as the supporting electrolyte. During the treatment, every predetermined time intervals, 5mL of samples were withdrawn from the catholyte for analysis.

The applied current density is a key experimental parameter that affects the electrochemical degradation process as it regulates the capability of hydroxyl radical generation on the electrode surface [42]. Initial experiments were done in the experimental unit with current densities of 4, 6, 8, 10 and 15 mA cm^{-2}, for a reaction time of 2 h. Fig. 7 (A–C) present plots of formaldehyde, TOC and COD concentrations as a function of electrolysis time. Initial formaldehyde concentration was 150 mg L^{-1}, COD was 360mg L^{-1}, TOC was 240mg L^{-1}.
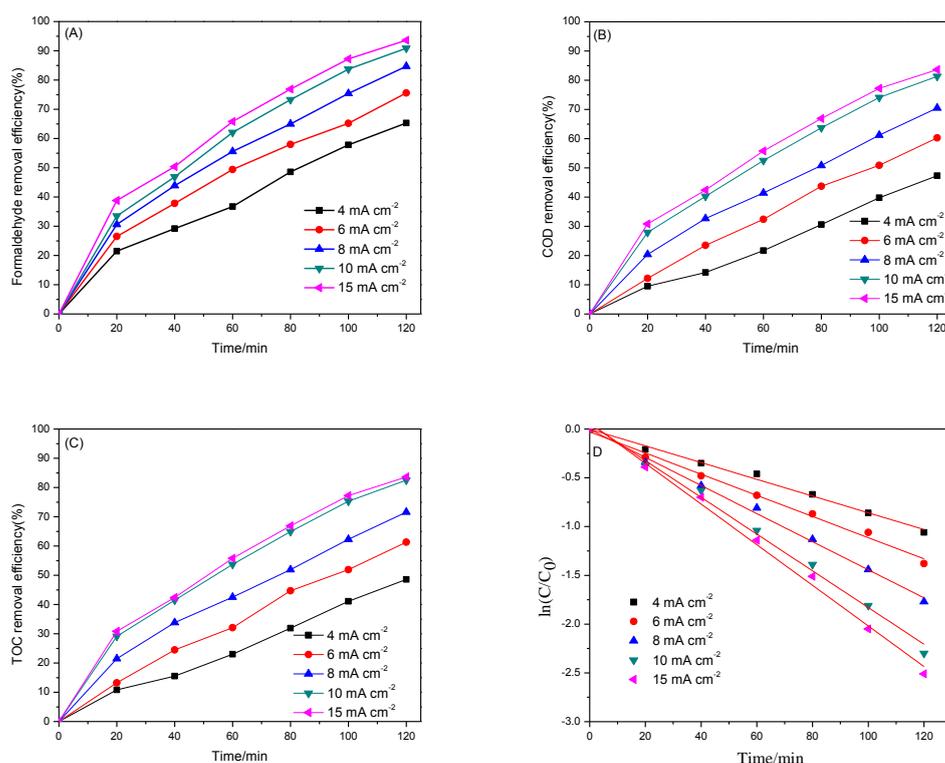

Figure 7. Removal efficiency of formaldehyde, COD and TOC on Pd/GO/GE (A-C) and kinetics of formaldehyde degradation (D). Initial concentration of formaldehyde: 0.05mol L^{-1}. Supporting electrolyte: 0.5mol L^{-1} Na2SO4. Initial pH: 4

To facilitate comparison, concentration values were normalized respective to initial concentrations. The plots reveal that the formaldehyde, TOC and COD have similar decaying curves. Initial concentrations of the formaldehyde, TOC and COD value diminish along with electrolysis proceeds, and there is a positive effect caused by the increase of current density, in which the higher the current density, the faster the three parameters under study decrease. The formaldehyde degradation efficiency, the COD removal efficiency and the TOC removal efficiency were 52.3%, 47.3% and 48.6% at 120 min when 4mA cm^{-2} current density was applied. While the current density was improved to 15mA cm^{-2}, the removal efficiency was significantly increased and almost all

formaldehyde was removed after 120 min. The COD removal efficiency and the TOC removal efficiency also reached 83.6% and 85% when the current density was 15mA cm^{-2} and the electrocatalytic time was 120 min. However the formaldehyde, COD and the TOC removal efficiency of the Pd/graphite were just 78.7%, 70.9%, 70.6% (Table 2) when the current density was 15mA cm^{-2}. This result is due to the higher electrochemical active surface area of the modified electrode. This result also indicated that the presence of GO greatly enhanced the active surface areas of Pd particles deposited on graphite. This is relevant to the cyclic voltammograms result (Fig. 4). The results illustrate that the Pd/GO/GE has higher degradation removal efficiency, also demonstrating the advantage of the present GO based electrode.

Table 2. Comparison of the removal efficiency of Pd/GO/GE with Pd/GE after 120 min electrolysis with a 0.5 mol L^{-1} Na$_2$SO$_4$ at a current density of 15 mA cm^{-2}

Electrodes	The formaldehyde removal efficiency(%)	The COD removal efficiency(%)	The TOC removal efficiency(%)
Pd/GE	78.7	70.9	70.6
Pd/GO/GE	90.6	83.6	85

3.4.2 Effect of initial solution pH

Solution pH is one of the important factors that affect the performance of electrochemical oxidation process [49]. The effect of pH value on electro-oxidation efficiency differs and always depends on the material of electrode[50]. To investigate the effect of pH values on electrooxidation of formaldehyde process, we studied the degradation of formaldehyde on Pd/GO/GE at different initial pH values which were adjusted with 0.1M H$_2$SO$_4$ and 0.1M NaOH. It was found that the removal efficiency of formaldehyde, COD and TOC was higher in acid or alkaline conditions than in neutral solution (Fig. 8). The maximum removal efficiency of formaldehyde, COD and TOC was observed at pH 4, which were 19.1%, 20.3% and 17.5% higher than that obtained at pH 7. As shown in Table 3, the rate constant (κ) value at initial pH value of 4 was about 2.3 times higher than that at pH 7, suggesting that the degradation process was more favorable in acidic solution. The following two mechanisms were proposed to explain the trend observed for the different pH values: (1) The oxidation potential of hydroxyl radical was higher in acid condition than in alkaline condition [47], thus the low pH inhibited the faster transfer process and caused improvement formaldehyde degradation efficiency. (2) High acidity enhanced free radical formation, therefore organic matter was easily oxidized [46].
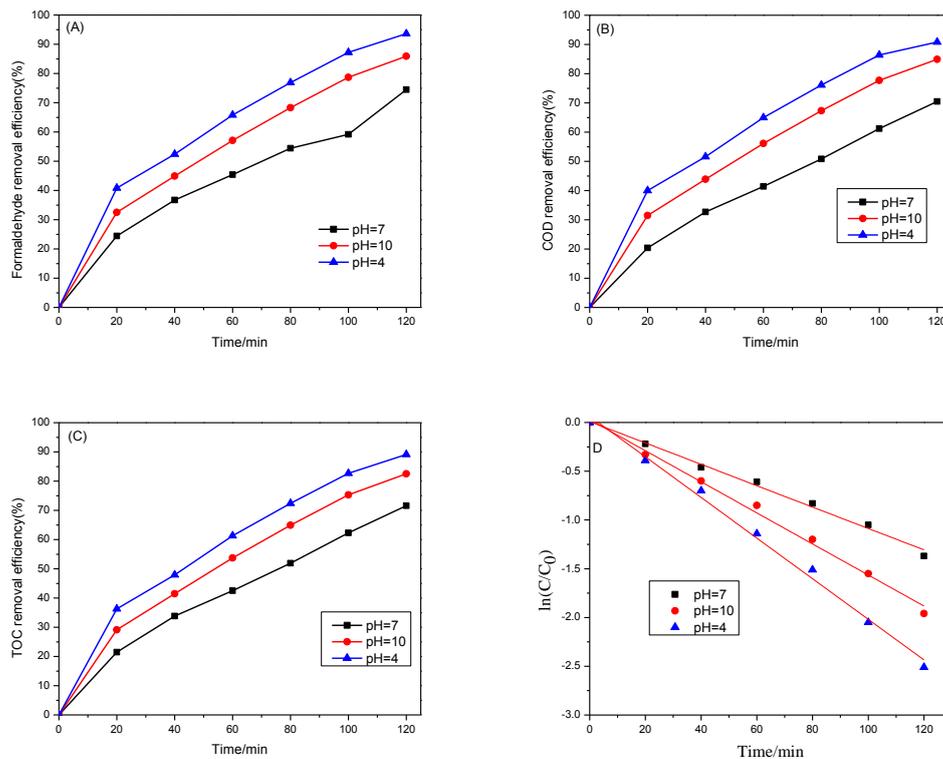
Figure 8. Removal efficiency of formaldehyde, COD and TOC on Pd/GO/GE (A-C) and kinetics of formaldehyde degradation (D)by applying different pH. Current density: 15 mA cm^{-2}. (Supporting electrolyte: 0.5M Na$_2$SO$_4$. Initial concentration of formaldehyde: 0.04M).

Table 3. Effect of current density, initial formaldehyde concentration, initial pH on pseudo first order rate constant(κ) results for the electrochemical degradation of formaldehyde removal.

Parameters		Formaldehyde removal efficiency(%)	k/min^{-1}	R^2
	4	65.3	0.0084	0.9902
	6	75.6	0.0096	0.9918
Current density/	8	84.7	0.0137	0.9927
mA cm^{-2}	10	90.9	0.0149	0.9933
	15	93.6	0.0188	0.9958
Initial	30	52.3	0.0059	0.9917
formaldehyde	60	63.3	0.0079	0.9923
concentration /mg	90	80.5	0.0126	0.9930
L^{-1}	120	91.2	0.0151	0.9935
	150	93.6	0.0188	0.9958
pH	4	93.6	0.0188	0.9958
	7	74.5	0.0089	0.9916
	9	85.9	0.0139	0.9929

3.4.3 Effect of initial concentration of formaldehyde on the electrochemical degradation

From the application angle, it was important to investigate the effect of initial concentration of formaldehyde. Fig. 9 shows the removal efficiency of formaldehyde concentration, COD and TOC when the initial pH was 4 and the current density was 15mA cm^{-2}. It could be seen that all the removal efficiency of formaldehyde concentration, COD and TOC were increased with increasing the initial concentration of formaldehyde. For 120 min electrodegradation process, the formaldehyde removal efficiency was increased from 82.1% to 93.6% when the initial concentration of formaldehyde was increased from 30 mg L^{-1} to 150 mg L^{-1}. It is considered that under the certain current density, the amount of OH· produced in the electrolysis was a constant. In the electrocatalytic oxidation process, the controlling step is diffusion process. The increase of the initial concentration of formaldehyde improves the diffusion velocity, and thus enhancing the removal efficiency of formaldehyde. Moreover, the high concentration of formaldehyde is advantageous to the full occupation of adsorption sites on the electrode surface. As a result, the active sites on the electrode surface are fully employed, which increases the utilization level of active OH· produced from the electrode reaction. Hence, the current efficiency is pronounced at high initial concentration of formaldehyde.
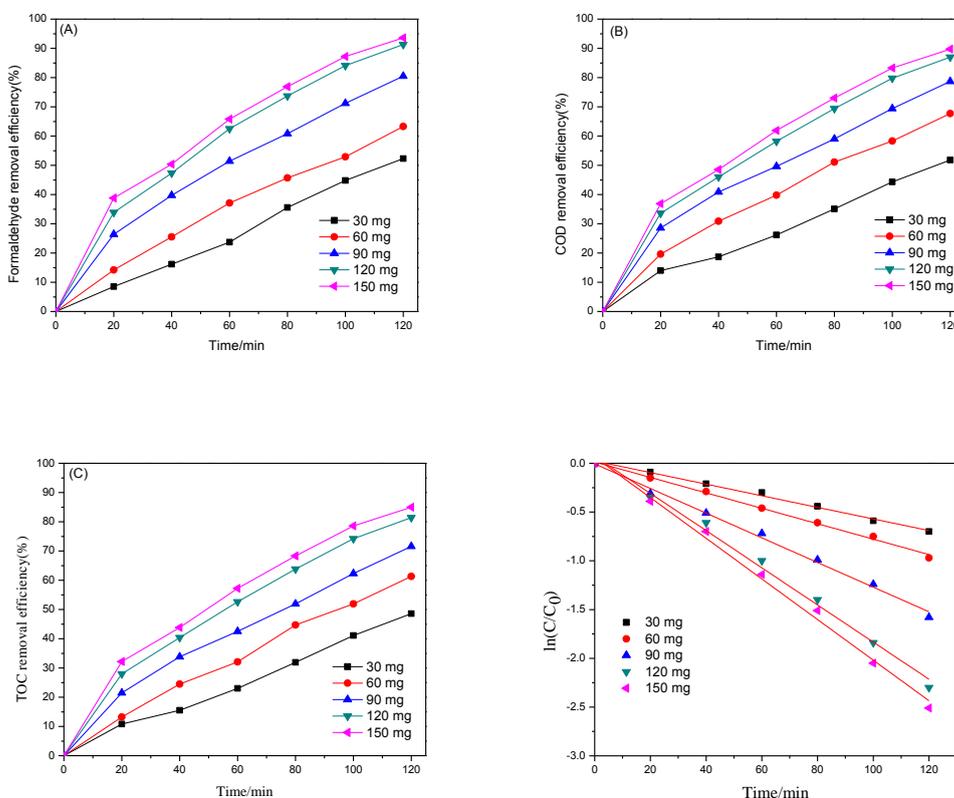

Figure 9. Removal efficiency of formaldehyde, COD and TOC on Pd/GO/GE electrode (A-C)   by applying different initial concentration of formaldehyde. Curren density: 15 mA cm^{-2}. Supporting electrolyte: 0.5M Na$_2$SO4. Initial pH: 4.

3.5 Electrocatalytic oxidation of higher concentration of formaldehyde

In the conventional methods of removing formaldehyde, a lot of technology has not good effect for high concentration of formaldehyde. Thus in a new experiment, a formaldehyde solution of higher concentration was subjected to electrolysis at 15 mA cm^{-2} and the pH was 4, initial formaldehyde concentration was 1500mg L^{-1}. In the Fig. 10, it can be seen that for 120 min electrodegradation process, the formaldehyde removal efficiency still can reach 64.4%, which demonstrate the electrode has high electrocatalytic performance and the electrochemical approach shows good removal effect for higher concentration formaldehyde.
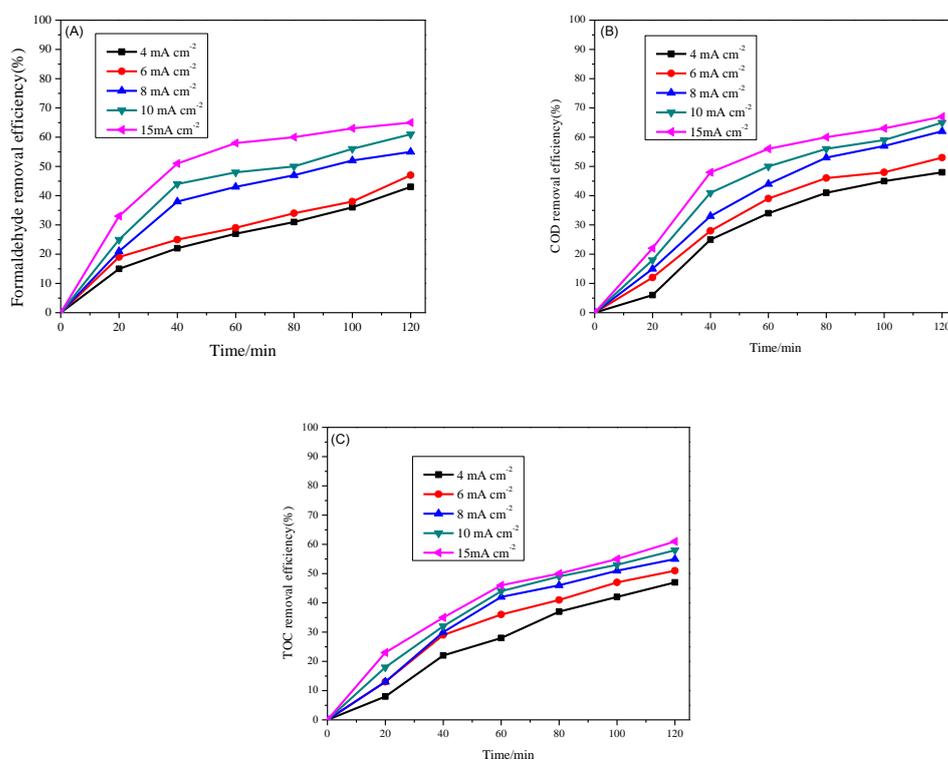

Figure 10. Removal efficiency of formaldehyde, COD and TOC on Pd/GO/GE electrode (A-C) by applying high formaldehyde concentration. Current density: 15 mA cm^{-2}. Supporting electrolyte: 0.5M Na$_2$SO$_4$. Initial concentration of formaldehyde: 1500 mg L^{-1}.

4. CONCLUSION

(1) A modified Pd/GO/graphite electrode was prepared successfully, characterized by SEM, EDS, XRD, XPS and cyclic voltammetry, the modified electrode had a good structure and electro-catalytic performance.

(2) The as-deposited Pd/GO/graphite modified electrode was applied to electro-degradation formaldehyde. When the electrolyte was 0.5 mol L^{-1} Na$_2$SO$_4$, current density was 15 mA cm^{-2}, initial concentration of formaldehyde was 150 mg L^{-1}, and initial pH was 4, the removal efficiency of formaldehyde, COD and TOC reached up to 90.6%, 83.6% and 85% for 2 h electrolysis.

(3) The degradation followed pseudo-first-order reaction process. Our work demonstrates the good prospect of the developed Pd/GO/graphite modified electrode for electrochemical degradation formaldehyde.

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