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Synthesis of Pd Nanoparticles Decorated with Graphene and Their Application in Electrocatalytic Degradation of 4-Chlorophenol

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Pd/graphene catalysts were prepared *in situ* from graphite oxide and palladium salts by the hydrogen-reduction method and were then used for the construction of Pd/graphene gas-diffusion electrodes (GDE). The prepared catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential pulse voltammetry (DPV) techniques. In the Pd/graphene catalysts, Pd particles, with an average size of 3.6 nm and an amorphous structure, were highly dispersed in the graphene. The Pd/graphene catalysts accelerated the two-electron reduction of O_2 to H_2O_2 by feeding air, which favors the production of hydroxyl radicals (HO[•]). In the electrolytic system, HO[•] was determined in the reaction mixture by the electron spin resonance spectrum (ESR). The dechlorination degree of 4-chlorophenol reached approximately 90.5% after 80 min, and the removal efficiency and the average removal efficiency of 4-chlorophenol, in terms of total organic carbon (TOC) after 120 min, reached approximately 93.3% and 85.1%, respectively. Furthermore, based on the analysis of electrolysis intermediates by high performance liquid chromatography (HPLC) and ion chromatography (IC), a reaction scheme was proposed for the Pd/grapheme GDE catalytic degradation of 4-chlorophenol.

Keywords: Electrocatalysis, Pd/Graphene Catalyst, 4-Chlorophenol, Degradation Mechanism.

1. INTRODUCTION

Chlorinated organic compounds, especially chlorophenols, have a significant impact on the environment and act as mutagenic or carcinogenic pollutants.^{1–3} Chlorophenols are easily introduced into the environment—primarily by the chemical and pharmaceutical industries—during the chlorination of municipal water or the degradation of other organic compounds. In natural water, chlorophenols pose a serious risk because of their persistence and accumulation in the environment. However, conventional treatments for decomposing chlorophenols, such as biological methods, are slow or non-destructive due to chlorophenols' resistance to biodegradation.⁴

Advanced oxidation processes have received substantial attention for their treatment of wastewater containing organic contaminants.^{5–8} Notably, using electrochemical oxidation for the treatment of wastewater has been widely investigated because of its ease of control, amenability to automation, high efficiency, and environmental compatibility.⁹⁻¹⁶ Of the various electrochemical processes that have been developed, electrochemical oxidation methods—such as anodic oxidation or the oxidation by electrogenerated oxidizing agents—have been the most extensively studied. Some high oxygen overvoltage anodes, such as boron-doped diamond, Ti/SnO₂, Ti/IrO₂, Ti/PbO₂, Ti/Bi₂O₅–PbO₂, and SnO₂, have been studied and showed potential for the degradation of 4-chlorophenol.^{17–21}

Very recently, indirect electro-oxidation methods have been developed for wastewater treatment involving H_2O_2 electrogeneration on the cathode. It has been reported that H_2O_2 can be electrochemically generated by reducing dissolved oxygen in an acidic solution:²²

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

Carbon materials, such as carbon/polytetrafluoroethylene,^{23–28} carbon nanotubes,²⁹ graphite,^{30–32} carbon

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felt,^{33–35} and reticulated vitreous carbon,^{36,37} are classified as highly conducting electrode materials for the electrochemical production of H2O2. Graphene, a one-atomthick two-dimensional monolayer of sp²-bonded carbon, has attracted a tremendous amount of attention from researchers³⁸ due to its unique properties and potential application in nanocomposites. Moreover, with its high surface area and chemical stability, graphene will be an important material in the design of next-generation catalysts with enhanced activity.^{39,40} The cooperative oxidation of active anodes and electrogenerated oxidant species on the cathode is expected to significantly increase the degradation rate of organic compounds.⁴¹ With a rationally designed electrochemical reactor, it is expected that organic degradation from both anodic oxidation and H_2O_2 oxidation (electrogenerated on the cathode) will be conducted in the same cell.

In this paper, the Pd/graphene catalyst used for the Pd/C gas-diffusion electrode system was prepared and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and differential pulse voltammetry (DPV) techniques. The degradation of 4-chlorophenol in an undivided electrolysis device with a self-made Pd/graphene gas-diffusion cathode and a Ti/IrO₂/RuO₂ anode was investigated. HO[•] was determined in the reaction mixture by the electron spin resonance spectrum (ESR). The degradation mechanism of 4-chlorophenol was also investigated in the Pd/graphene gas-diffusion electrode system. The purpose of this study was to use this system to demonstrate effective methods for the formation of hydroxyl radicals to completely oxidize 4-chlorophenol.

EXPERIMENTAL DETAILS Preparation of Pd/Graphene Catalyst and Gas-Diffusion Cathode

Graphite oxide (GO) was prepared from natural graphite flakes (99.99%, 325 mesh, Qingdao Zhongtian Company) according to a modified Hummers method.⁴² The Pd/graphene catalyst was prepared using the hydrogen-gas reduction method. Palladium chloride was first dissolved in a concentrated hydrochloric acid solution and then diluted with 15 mL of deionized water. The solution of PdCl₂ was added dropwise to a vigorously stirred GO solution at 80 °C. The mixture was kept at 80 °C for 2 h and was then evaporated to dryness. The dried catalyst was further reduced at 250 °C in a stream of hydrogen gas at a rate of 30 mL min⁻¹ for 2 h and was then cooled to ambient temperature under hydrogen atmosphere. A Pd/graphene catalyst with a Pd load of 1.0 wt.% was obtained and stored in a desiccator. The gas-diffusion electrodes were prepared according to the method described in a previous report.⁴³

2.2. Procedures

Electrolysis was conducted in a 100-mL undivided electrolysis device with a $Ti/IrO_2/RuO_2$ anode (16 cm²) and a

gas-diffusion cathode (16 cm²). A previous report contains a schematic diagram of the experimental setup.⁴⁴ A direct current laboratory power supply with a current–voltage monitor provided electric power. The experimental conditions were as follows: the initial 4-chlorophenol concentration was 100 mg L⁻¹; the current density was 39 mA cm⁻²; the concentration of the supporting electrolyte (Na₂SO₄) was 0.05 mol L⁻¹; the distance between electrodes was 2.0 cm; and the initial pH was 7.0. Before starting electrolysis, air was fed for 5 min to keep the electrolysis solution oxygen saturated. Furthermore, air was fed into the electrolysis device at a flow rate of 25 mL s⁻¹ until the end of the electrolysis process.

2.3. Analytical Methods

The XRD patterns were used to determine the identity of any phase present and their crystallite size. The Pd/C catalyst was characterized by XRD with a Rigaku D/max-IIIA X-ray power diffractometer using Cu K α radiation with an Ni filter. The Pd particle morphology and size distributions were determined by TEM (JEM-2010F TEM microscope) operated at an accelerating voltage of 200 kV.

The DPV spectra were recorded using a potentiostat/galvanostat (EG&G Model 273A) with a standard three-compartment cell consisting of a Pt wire as the counter electrode, an Ag/AgCl electrode as the reference electrode, and the Pd/graphene catalyst (or graphene) modified electrode as the working electrode. To prepare a catalyst ink 5 mL of Pd/graphene catalyst (or graphene) was suspended in a mixture of 1 mL of ethanol and 50 μ L of Nafion[®] solution (5 wt% Aldrich solution). Then, 10 μ L of ink was transferred with an injector to the surface of a clean glassy carbon disk electrode with an area of 0.126 cm^2 . After the ethanol evaporated, the electrode was heated at 75 °C for 10 min. A Na₂SO₄ solution with a 0.5 mol L^{-1} concentration was used as an electrolyte, which was saturated with oxygen (or nitrogen) by feeding oxygen gas (or nitrogen gas) to the cell for 30 min before the electrochemical measurement. Oxygen gas was continuously fed to the solution throughout the electrolysis process. The temperature was kept at 25 °C throughout the experiment. The scan rate was 100 mV s^{-1} .

The radicals were determined by ESR measurements, which were performed in the X-band on a JES-FE3AX ESR spectrometer (JEOL, Tokyo, Japan) at room temperature. The ESR spectrometer was set as follows: microwave frequency, 9.44 GHz; microwave power, 20 mV; modulation frequency, 100 kHz; modulation amplitude, 0.5 G; center field, 3367 G; scan width, 100 G; receiver gain, 2×10^3 ; time constant, 0.3 s; sweep time, 4 min. The ESR spin trapping agent was 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 11.1 mmol L⁻¹).

The determination of 4-chlorophenol and its stable degradation products in the electrolyzed solutions was carried out using high-performance liquid chromatography (HPLC, Waters, America) analyses by comparing their

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retention times with those of the standard compounds. Samples of 20 μ L, previously filtered with PTFE filters of 0.45 μ m, were injected into the HPLC. The separation was performed using a Znertisl ODS-SP C18 column (250 mm × 4.6 mm, 5 μ m) at a flow rate of 1.0 mL/min and at a column temperature of 30 °C. The aromatic compounds were determined by HPLC, running with a mobile phase of methanol/water (v/v) at 80/20 and an UV detector set at a wavelength of 280 nm, except for benzoquinone, whose concentration was measured at 254 nm. The carboxylic acids were determined by HPLC, running with a mobile phase of methanol/KH₃PO₄ 25/75 (v/v) at pH = 2.1 adjusted with H₃PO₄ and an UV detector set at 210 nm.

Small molecular carboxylic acids and the concentration of chloride ions in the electrolyzed solutions were determined using ion chromatography (ICS-3000, Dionex, America) by comparing the retention times of the standard compounds. Samples of 30 μ L, previously filtered with PTFE filters of 0.45 μ m, were injected into the IC. The separation was performed using an AS-11 column at the flow rate of 1.2 mL min⁻¹. The column temperature was 30 °C. The mobile phase consisted of 5% (vol.) 5 mmol L⁻¹ NaOH and 95% (vol.) deionized water in the 0–6 min period; the volume of NaOH was increased to 12% in the 6–41 min period, reduced to 5% in the 41–42 min period and remained at 5% in the 42–50 min period.

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3. RESULTS AND DISCUSSION Pyright: American S

3.1. Characterization of the Pd/Graphene Catalyst

The XRD patterns of graphite, GO, and Pd/graphene catalysts are shown in Figure 1. The initial graphite powder showed a typical sharp diffraction peak at $2\theta = 26.6^{\circ}$ with the corresponding *d*-spacing of 3.36 Å. The sharp diffraction peak revealed that the hexagonal system crystal structure of graphite was stable. After chemical oxidation, a lower broad peak, compared to the XRD pattern of original graphite, appeared at $2\theta = 12.1^{\circ}$, indicating the

Graphite Graphite Go GO Pd/graphene

Figure 1. XRD patterns of the graphite, GO and Pd/graphene catalysts.

50

2theta (degrees)

60

70

80

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40

10

20

30

successful formation of graphite oxide. The d-spacing of graphite oxide was 7.34 Å, indicating that the order of the layers had been disrupted. Oxygen functional groups were inserted into the interplanar crystal spacing, resulting in an increase in the distance between carbon sheets. This larger distance between the GO sheets shifted the XRD peak to smaller angles, causing the low broad peak presented at 12.1°.45 After using hydrogen gas to reduce the GO, the XRD of the resulting graphene material showed that the 12.1° peak had disappeared, confirming that the reduction of the GO sheets did in fact occur.⁴⁶ The appearance of a new, small, broad peak at approximately $2\theta = 25^{\circ}$ with a corresponding d-spacing of 3.82 Å in the Pd/graphene suggested the presence of a minor component of multilayer graphene.⁴⁷ This pattern was in contrast to the peak patterns of the graphite and the GO, which were low and broad because the formed metal nanoparticles prevent the restacking of carbon sheets⁴⁸ and enlarge the interlayer spacing. The peak at approximately 40° was characteristic of a diffraction peak of face centered-cubic crystalline Pd and corresponded to its (111) planes. The average size of the metal particles, calculated from the Pd (111) diffraction line using the Scherrer formula, was 3.6 nm.

The TEM image (shown in Fig. 2) of the Pd/graphene catalyst and its metal particle size was measured to estimate the geometry and the particle size of the Pd species. No obvious aggregation was detected from the images. The TEM analysis showed a homogeneous distribution of Pd nanoparticles at the graphene surface, with an average particle size of 3.66 ± 0.25 nm. This result helps confirm the XRD result.

Figure 3 shows the DPV curves of the catalyst electrode surface of different gases in a 0.5 mol L^{-1} Na₂SO₄ solution (pH = 12.8 adjusted with NaOH solution). There was a high reduction peak (Pd/graphene, graphene: O₂) at about -0.38 V when oxygen was present in the basic solution. However, this peak disappeared when the oxygen was



Figure 2. TEM image of Pd/graphene.

0.60

0.55

0.50

0.45

0.40

0.35

0.30

-1.5

I (mA)



Figure 3. DPV curves of the catalyst electrode surface using different gases.

E (V)

absent (Pd/graphene: N_2). According to the redox potential, the two-electron reduction of O_2 to peroxide anion (H O_2^-) led to the formation of reduction current peaks using catalyst-modified electrodes in a basic solution in the presence of oxygen gas. The reduction current peak of the Pd/graphene catalyst modified electrode was higher than that of the electrode modified without catalyst. The reduction was attributed to the Pd/graphene catalyst, which accelerated the two-electron reduction of O_2 to H_2O_2 .

3.2. Hydroxyl Radical Electrogenerated on the merican Pd/Graphene Gas-Diffusion Electrode System

The Ti/IrO₂/RuO₂ anode was used herein. A direct anodic electrochemical oxidation process, by $MO_x(OH^*)$ or MO_{x+1} produced on the anode surface, was involved in the degradation of 4-chlorophenol on the anode.⁴⁹ Furthermore, the gas-diffusion cathode catalyzed the two-electron reduction of O₂ to H₂O₂, which may be further converted to HO^{*}:⁵⁰

$$\mathrm{H}_{2}\mathrm{O}_{2} + e^{-} \to \mathrm{OH}^{-} + \mathrm{HO}^{\bullet}$$
(2)

The ESR was used to quantitatively determine the free radicals in an undivided electrolysis device. Figure 4 shows the change of the HO''s relative intensityconcentration with the electrolysis time, as well as the typical ESR spectrum obtained after 15 min electrolysis in the DMPO solution (inset). The spectrum was composed of quartet lines with a peak height ratio of 1:2:2:1. The ESR parameters (hyperfine constants $a_{\rm N} = a_{\rm H} = 14.0$ G and g-value = 2.0065) coincided with those of the DMPO-OH[•] adduct, as demonstrated previously,⁵¹ confirming that the quartet signal was DMPO-OH' adduct. The adduct peak in the Pd/graphene catalyst modified electrode system can be attributed to the presence of HO'. The HO' concentration matched the intensity of the adduct peak. The HO' concentration rose as the electrolysis time increased, reaching its maximum after 25 min of electrolysis. This trend indicated that the Pd/graphene catalyst in the Pd/graphene



Figure 4. Relative intensity and ESR spectra of HO' radicals trapped by DMPO in the electrolysis device. Concentration of DMPO: 11.1 mmol L^{-1} ; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L^{-1} ; current density: 39 mA cm⁻².

gas-diffusion electrode system accelerated the two-electron reduction of O_2 to H_2O_2 when air was fed into the cell, which favored the production of HO[•] (see Figs. 3 and 4). In the following experiments, the electrochemical degradation of 4-chlorophenol was investigated in an undivided electrolysis system, fed with air, using Pd/graphene gas-diffusion cathodes.

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3.3. Electrochemical Oxidation of 4-Chlorophenol

Changes in the UV absorption spectrum of 4-chlorophenol with electrolysis time (0, 20, 40, 60, 80, 100, and 120 min) are shown in Figure 5. The result indicated that 4-chlorophenol has significant UV absorption at 225 nm and 280 nm. The spectrum maximums of 4-chlorophenol



Figure 5. The analysis of 4-chlorophenol by UV scanning at different electrolysis times. Concentration of 4-chlorophenol: 100 mg L⁻¹; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L⁻¹; current density: 39 mA cm⁻².

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Figure 6. Removal of 4-chlorophenol and variations of TOC with electrolysis times by the Pd/C gas-diffusion electrode system. Concentration of 4-chlorophenol: 100 mg L^{-1} ; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L^{-1} ; current density: 39 mA cm⁻².

at 225 nm and 280 nm were reduced as the electrolysis time decreased. This reduction indicated that the concentration of 4-chlorophenol in the Pd/graphene gasdiffusion electrode system decreased as the electrolysis time increased. There are no obvious absorption peaks after 120 min of electrolysis. The absorption peak for benzoquinone (245 nm) appeared during the electrolytic process. The color of the electrolyte in the anodic compartment turned from colorless to yellow, which demonstrated that the benzoquinone was accumulated during the electrolytic process. The degradation of 4-chlorophenol was attributed to the cooperative oxidation processes, including direct and/or indirect electrochemical oxidation at the anode and H_2O_2 and HO[•] produced by the reduction of oxygen at the cathode.

Figure 6 shows the removal efficiency of 4-chlorophenol and TOC, and the electrolysis time in the Pd/graphene gas-diffusion electrode system. The removal efficiency of 4-chlorophenol increased from 35.3% to 93.3% when the electrolysis time was extended from 20 min to 120 min. However, the TOC removal efficiency varied from 31.9% to 85.1% during the same period. During the electrolysis process, the total TOC removal was lower than the corresponding degradation fraction of the target 4-chlorophenol. This trend indicated that most of the 4-chlorophenol was oxidized to intermediates, which were not further oxidized to CO₂ and H₂O.

3.4. Identification of Intermediates and Their Evolution

The changes in the concentration of chloride ions with electrolysis time during the degradation process of 4-chlorophenol throughout the electrolysis process are illustrated in Figure 7(a). The initial solutions of 4-chlorophenol contained the dissociative chloride ion. The chloride ion concentration of 4-chlorophenol





Figure 7. Change of the intermediate concentrations during the electrochemical oxidation of 4-chlorophenol. Concentration of 4-chlorophenol: 100 mg L^{-1} ; concentration of supporting electrolyte (Na₂SO₄): 0.05 mol L^{-1} ; current density: 39 mA cm⁻².

increased as the electrolysis time increased. The concentration of chloride ions reached its maximum after 80 min, and the degree of dechlorination reached approximately 90.5%. As the electrolysis time increased, the concentration of chloride ions decreased. This trend indicated that the chloride ion was already oxidized to Cl_2 at the anode. Similar findings were reported for the electrolysis of chlorophene with a BDD anode,⁵² and Cl_2 was immediately driven away from the reaction system.⁵³

These intermediates were unequivocally identified by comparing their retention times and UV-Vis spectra with those of pure compounds. Figure 7 shows the evolution of the soluble species detected during the degradation of 4-chlorophenol. A fast formation and destruction of the main intermediates can be observed. Figure 7(a) shows that the concentration of the primary product of hydroquinone, benzoquinone, increases in the first 60 min and then begins to decrease until its complete removal by the 120 min marker. The hydroxylated derivative benzoquinone reached its peak concentration at approximately 80 min and then fell to below its detection limit at 120 min. Through the HPLC and IC analyses, the main intermediates after 60 min were aliphatic carboxylic acids (maleic, fumaric, succinic, malonic, acetic, and formic acids). As shown in Figure 7(b), maleic, fumaric and succinic acids attained their maximum concentrations at 80 min and were quickly degraded to malonic, oxalic and formic acids, respectively. After 120 min, most of the aliphatic carboxylic acids were transformed into carbon dioxide and water. These results indicate that all of the aromatic intermediates were transformed into carboxylic acids because they reacted rapidly with the $MO_x(OH^*)$ or MO_{x+1} produced on the anode surface and the H_2O_2 and HO* produced by the reduction of oxygen at the cathode.

Figure 8 presents a pathway for the degradation of 4-chlorophenol by the Pd/graphene gas-diffusion electrode system. The degradation pathway is proposed as follows: an HO' attacks at the C(4)-position of 4-chlorophenol yields hydroquinone with the loss of Cl⁻. Hydroquinone is subsequently dehydrogenated to benzoquinone. The oxidation of benzoquinone, after the ring opening, leads to the formation of aliphatic carboxylic acids such as maleic acid and fumaric acid, which are degraded to succinic and malonic acid and then form acetic and formic acid. The final products are carbon dioxide and water. The degradation reaction of 4-chlorophenol in the electrolysis device is believed to be cooperative oxidation, by direct or indirect electrochemical oxidation at the anode and HO₂, HO[•] produced by oxygen reduction at the cathode. Because of its low current efficiency in practical use, it was not necessary



Figure 8. Reaction pathway for the electrochemical oxidation of 4-chlorophenol.

to degrade 4-chlorophenol to the final products of CO_2 and water. It may be more worthwhile to treat 4-chlorophenol to its biodegradable stage-aliphatic carboxylic acids and then seek an economically viable biological process.

4. CONCLUSIONS

A Pd/graphene gas-diffusion cathode that generated H_2O_2 by a two-electron reduction of oxygen gas fed to the cathode was prepared and used to degrade 4-chlorophenol in an undivided electrolysis device. In the Pd/graphene catalyst, Pd particles with an average size of 3.6 nm were highly dispersed in the graphene with an amorphous structure. This characteristic indicates that the Pd/C catalyst in the Pd/C gas-diffusion electrode system accelerated the two-electron reduction of O_2 to H_2O_2 in the presence of air, which favors the production of HO'. In the Pd/graphene gas-diffusion electrode system, the dechlorination degree of 4-chlorophenol reached approximately 90.5% after 80 min, and the removal efficiency and the average removal efficiency of 4-chlorophenol, in terms of total organic carbon (TOC) after 120 min, reached approximately 93.3% and 85.1%, respectively. The main intermediate of the 4-chlorophenol dechlorination was determined to be hydroquinone. Hydroquinone was subsequently dehydrogenated to benzoquinone. The further oxidation of benzoquinone, after ring cleavage, led to the formation of aliphatic carboxylic acids, such as maleic, fumaric, succinic, malonic, acetic and formic acids.

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