

Electrocatalytic Hydrogenation of 4-Chlorophenol on the Glassy Carbon Electrode Modified by Composite Polypyrrole/Palladium Film

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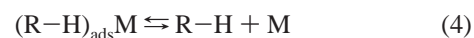
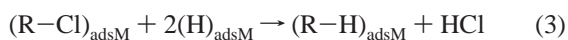
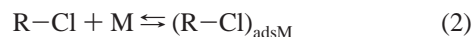
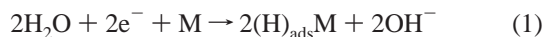
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A polypyrrole/palladium composite film was prepared on a glassy carbon electrode by the electrochemical deposition method. The palladium particles were uniformly dispersed on a polypyrrole film that was previously electrodeposited on a glassy carbon electrode. By controlling the polymerization process of pyrrole, a highly porous polypyrrole film was obtained; this kind of structure provided more surface areas for depositing palladium particles. The sizes of Pd particles deposited on the porous polypyrrole film are about 15–30 nm. The X-ray photoelectron spectroscopy results showed there was strong interaction between polypyrrole film and palladium particles. This modified electrode showed excellent current efficiency (49.5%) for electrochemical hydrogenation of 4-chlorophenol and the phenol was the sole product. The potential effect on the dechlorination process was also investigated.

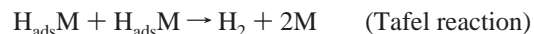
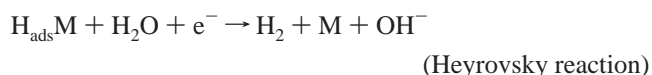
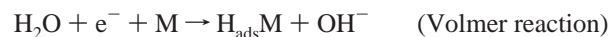
Introduction

Electrocatalytic hydrogenation (ECH) is a process in which chemisorbed hydrogen is generated at the electrode surface by electrolysis of water. ECH is a very useful tool for the hydrogenation and hydrogenolysis of organic molecules. The former involves the addition of hydrogen to π bonds, whereas the latter involves the reductive cleavage of σ bonds, as in dechlorination reactions. As an electrochemical process, ECH is a green technology, which employs ambient temperatures, aqueous media, and electrons rather than chemical additives to promote chemical change. The use of ECH for the dechlorination of chloroaromatic compounds is potentially advantageous compared with traditional techniques such as adsorption on activated carbon or incineration. Recent studies have shown that the dechlorination of 4-CP (4-chlorophenol) by electrocatalytic hydrogenation on a palladized carbon cloth and of chlorophenoxy acetic acids on palladium-loaded carbon felt can be performed with good efficiencies.^{1–3} According to the literature,^{3,4} the mechanism of the electrocatalytic hydrogenolysis of a carbon–halogen bond involves the steps described in eqs 1–4.



From the above equations, we can see there are four reaction steps in the hydrodechlorination: (I) the formation of chemisorbed hydrogen on the metal surface, (II) the adsorption of chlorophenols with the metal surface, (III) the reaction between metal chloride and chemisorbed hydrogen, and (IV) the regeneration of metal surface. ECH always competes with the

HER (hydrogen evolution reaction), which proceeds either via the Volmer–Heyrovsky or via the Volmer–Tafel mechanism.



Because of its strong ability to intercalate hydrogen in its lattice, the palladium is the most common catalyst for ECH. It was shown to be much more effective in promoting the dechlorination reaction than platinum and Raney nickel.^{1,4} Usually, a high degree of dispersity and the large surface areas of palladium are desirable for the ECH process. High surface areas of many conducting polymers favored their use as supporting materials for the development of new electrocatalysts.⁵ Because of relatively high electric conductivity of some polymers, it is possible to shuttle the electrons through polymer chains between the electrodes and dispersed metal particles where the electrocatalytic reaction occurs. Thus, an efficient electrocatalysis can be achieved at these composite materials. A great deal of attention was paid to the use of conducting polymers as supporting matrixes for the immobilization of catalytically active noble metal particles.^{6–8} Considerable interest has recently been devoted to conducting polymers based on the pyrrole ring ($\text{C}_4\text{H}_5\text{N}$). Large flexible Ppy (polypyrrole) films of good environmental stability can be prepared electrochemically.^{9,10} The Ppy film is used to physically separate the catalytic particles and decrease their agglomeration rate. Meanwhile, the Ppy film is believed to modify the electronic nature of the metal particles as well, thus affecting their chemisorptive and catalytic properties. The enhancement of surface catalytic activity by the metal–support interaction as well as the large surface area achieved with low loading levels makes such a system attractive for the application in the electrochemical dechlorination. The objective of our work is to use the electrodeposition method to

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disperse small palladium particles on a polypyrrole film, which was previously electrodeposited on a glassy carbon electrode from an aqueous acid solution. This kind of modification typically concerns the insertion of small Pd particles into the Ppy film after the polymerization process. Thus, the polypyrrole film is expected to have a highly porous structure for providing high surface areas. To reach this goal, we prepared the polypyrrole film in the presence of surfactant (sodium dodecyl sulfate) during the electropolymerization of Ppy. Surfactants in solution spontaneously aggregate at solid–liquid interfaces due to surface forces (i.e., electrostatic interaction between the surfactant headgroup and the surface charge). Choi reported the preparation of a thin mesoporous platinum film by utilizing potential-controlled SDS assembly.¹¹ We want to obtain a highly porous structure of polypyrrole film mediated by surfactant in order to deposit highly dispersed palladium particles. Compared with the simple Pd film electrodeposited on the glassy carbon electrode, this modified film electrode is expected to provide more reducing species of Pd–H and thus enhance the surface electrocatalytic properties (faster kinetics) of the electrode for the dechlorination of 4-CP (4-chlorophenol) in aqueous solution at ambient temperature.

Experimental Section

Film Preparation and Characterization. A conventional undivided cell was used in the preparation of the Ppy film and the Ppy/Pd composite film. All the electrochemical measurements were performed with an EG&G 273 potentiostat/galvanostat controlled by M270 software. The counter electrode was a platinum foil ($2.0 \times 1.5 \text{ cm}^2$) while the reference electrode was $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{SO}_4^{2-}$. The working electrode in the electrochemical studies was a GC (glassy carbon) plate ($2.00 \times 1.50 \times 0.20 \text{ cm}^3$, Johnson Matthey). Prior to each experiment, the glassy carbon electrode was sequentially polished with 1.0, 0.3, and $0.05 \text{ }\mu\text{m}$ alumina, until a shiny, mirrorlike surface was obtained. Then it was placed under ultrasonic conditions in water and methanol for 10 min. The polypyrrole films were prepared from an aqueous solution containing 0.1 M pyrrole (Aldrich) and 0.05 M H_2SO_4 with or without 1% sodium dodecyl sulfate at a constant current of $0.5 \text{ mA}/\text{cm}^2$ for 8 min. Pyrrole was distilled prior to use. All other chemicals were used as received. The small Pd particles were electrodeposited on Ppy films from an aqueous solution containing $2.24 \times 10^{-3} \text{ M}$ PdCl_2 (99.5% Beijing Chemical Company) and 2.0 M HCl at a constant current of $0.75 \text{ mA}/\text{cm}^2$ for 10 min. We also prepared the GC/Pd electrode under the same condition to compare with the GC/Ppy/Pd electrode. The Ppy film and Ppy/Pd composite film were characterized by SEM (scanning electron micrograph), CV (cyclic voltammetry), and XPS (X-ray photoelectron spectroscopy), and all water was of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ quality obtained from a Millipore-Q system. A JEOL JSM 6500F scanning electron microscope was used to observe the morphology of the films. For XPS measurements, a Physical Electronics PHI5300ESCA/610SAM with monochromatized Al $\text{K}\alpha$ radiation and an energy resolution of 0.5 eV was used.

Dechlorination of 4-Chlorophenol by the ECH Process. For the bulk electrolysis of 4-CP solution, a two-compartment electrolytic cell separated by a cation-exchange membrane (Nafion-324, E. I. duPont de Nemours & Co.) was used to avoid oxidative destruction of the 4-CP on the anode and chlorination of the products by generated Cl_2 . The modified electrode described above was used for constant current electrolysis of 4-CP at ambient temperature. Identification of the dechlorinated products was made by high performance liquid chromatography

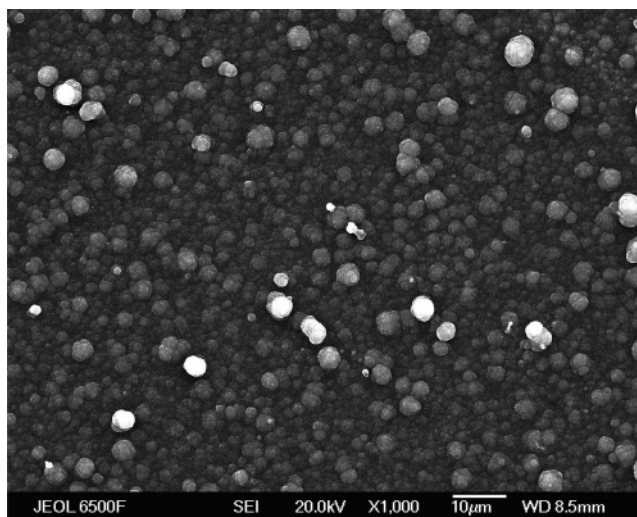


Figure 1. SEM image (magnification 1 000 \times) of the surface of a Ppy film.

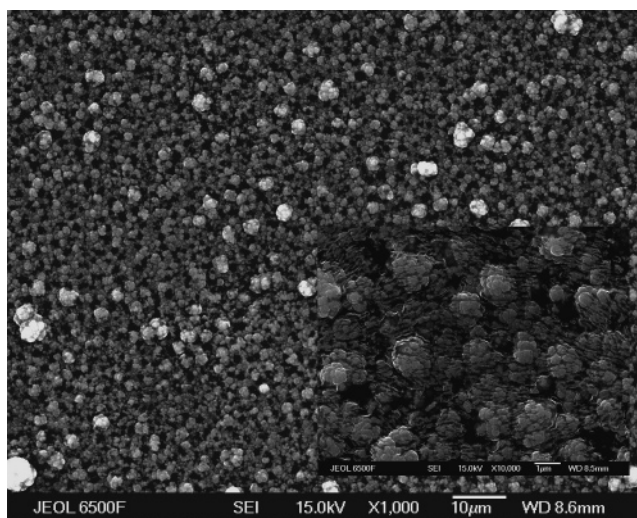


Figure 2. SEM image (magnification 1 000 \times) of the surface of a Ppy film mediated by SDS. Insertion: magnification 10 000 \times .

(HPLC Waters 600, 4.6 mm \times 250 mm Zorbax SB-C18 column, UV absorbance set at 254 nm, mobile phase composition 30/70 water/methanol mixed by volume). Phenol, 4-chlorophenol peaks were characterized by using standard solutions. Quantification of the products was accomplished by the use of a calibration curve.

Results and Discussion

Film Morphology. Polypyrrole deposited on GC electrodes was a dark green film; the morphology of the Ppy film has been investigated by SEM. For the Ppy film not mediated by SDS, the image (Figure 1) revealed that the Ppy film surface consists of a random distribution of globular features (grains). The individual grains are spherical with the average diameter of 3–5 μm , which can be easily recognized over the surface. For the Ppy film mediated by SDS, the image (Figure 2) showed a highly porous structure totally different from the morphology of the Ppy film reported. In the low magnification (1 000 \times), it seemed like a net with ordered nodules and pores. The pores are about 1 μm . In the high magnification (10 000 \times), we can see the highly porous structure of the nodules (see the insert in Figure 2); however, these pores are disordered. The pores' ends are about 50–100 nm. The sizes of small Pd particles deposited

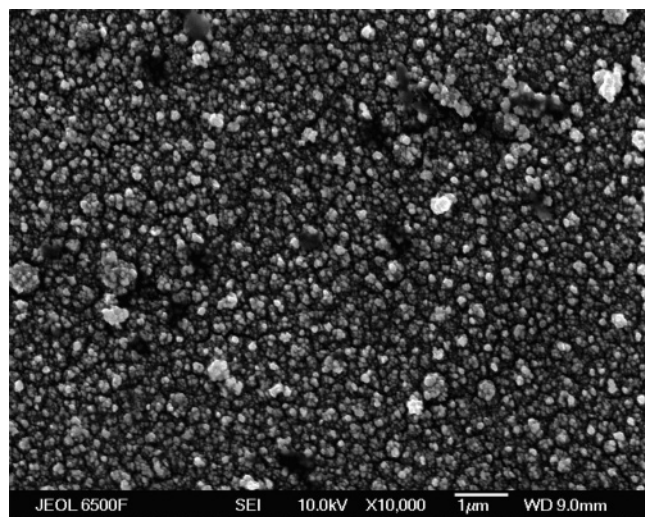


Figure 3. SEM image (magnification 10 000 \times) of the surface of Pd particles electrodeposited on the Ppy film.

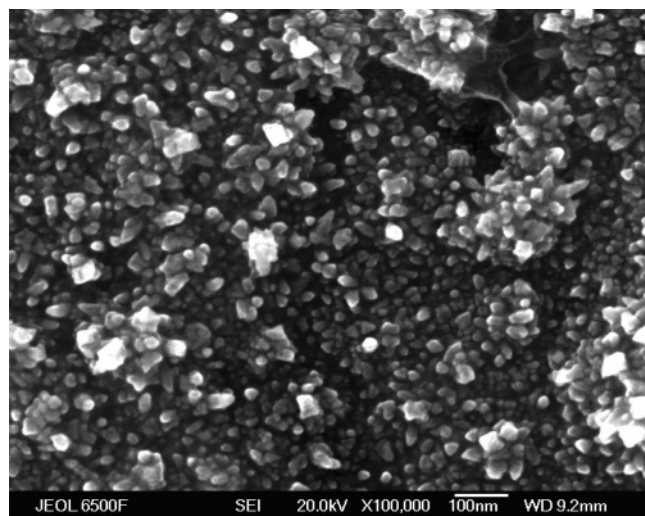


Figure 4. SEM image (magnification 100 000 \times) of the surface of Pd particles electrodeposited on the Ppy film mediated by SDS.

on film were also characterized by SEM (Figures 3 and 4). The Pd particles on the Ppy film not mediated by SDS are 100–200 nm while the Pd particles on the Ppy film mediated by SDS are 15–30 nm. We believe the highly porous structure of the Ppy film provides more surface areas for depositing smaller Pd particles. Thus the sum of the surface area of deposited Pd particles is higher.

Cyclic Voltammetry of the Polypyrrole Film and the Polypyrrole/Palladium Film. The electrochemical properties of different morphologies of the Ppy film were investigated by cyclic voltammetry in 0.1 M H₂SO₄. All samples demonstrated electrochemical activity, which was characterized by typical reduction and oxidation response. The porous Ppy(SDS) films have considerably higher redox current than the normal Ppy film (see Figure 5). The difference in redox currents reflects the effective active surface areas that are accessible to the electrolytes. Apparently, the porous Ppy(SDS) films have higher effective surface areas, which are desirable for supporting electrocatalysts. After depositing Pd particles, all electrodes showed typical H adsorption peaks and H desorption peaks from -0.7 to -0.35 V. The H adsorption peak currents of the GC/Pd and GC/Ppy/Pd and GC/Ppy(SDS)/Pd are -15 , -24 , and -43 mA, respectively (see Figure 6). From the current measure-

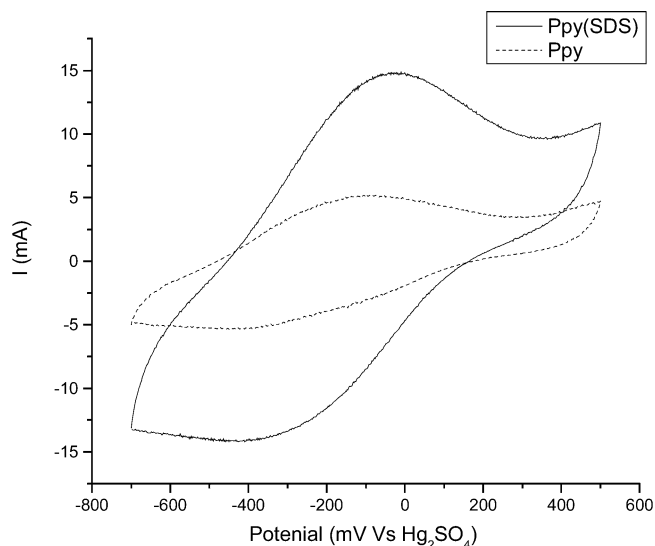


Figure 5. Cyclic voltammograms of GC/Ppy electrodes in 0.5 M H₂SO₄, scan rate 50 mV/s.

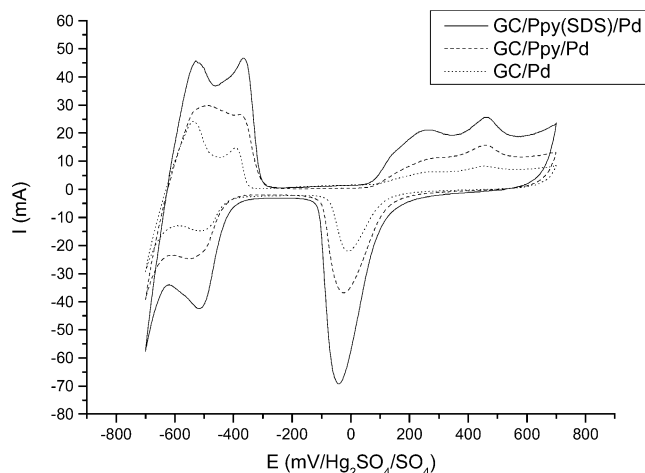


Figure 6. Cyclic voltammograms of three electrodes in 0.5 M H₂SO₄, scan rate 50 mV/s.

ments, it is clear that the H adsorption current of the GC/Ppy(SDS)/Pd electrode is much higher than that of the GC/Ppy/Pd electrode and the GC/Pd electrode. The remarkably high H adsorption current is directly related to the high surface areas of Pd particles. Therefore, high surface areas of Pd particles were obtained through preparing the Ppy(SDS)/Pd composite film. The stability of the Ppy(SDS)/Pd film in acid media was also investigated by CV 20 times a day successively for one month—there was negligible change in the shape and height of the current of H adsorption/desorption areas, indicating the film had high electrochemical stability. Furthermore, this film was very hard to remove from the GC electrode surface. The only way to remove the film was to polish the electrode mechanically, indicating a high mechanical stability.

XPS Study of the Ppy Film and the Ppy/Pd Film. A N1s spectrum of Ppy(SDS) can be seen in Figure 7—the peak is asymmetric on the high binding energy wing of the main polypyrrole peak at 399.6 eV. Ppy has a significant overlap of delocalized π -electrons along the polymer chain, but this is itself insufficient for electrical conductivity, for which redox perturbation of the polymer chain is necessary. Thus oxidation, the most common procedure, produces an electron-deficient polycationic chain, requiring the uptake of anions from the surrounding medium for charge compensation. These ions produce electric

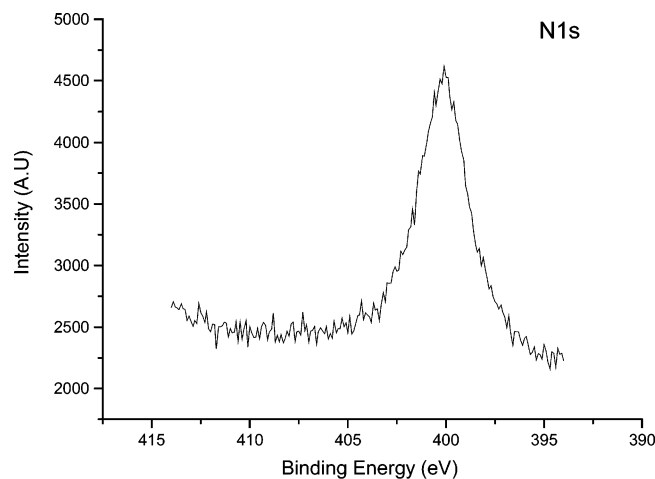


Figure 7. N1s binding energy of N species on the Ppy film.

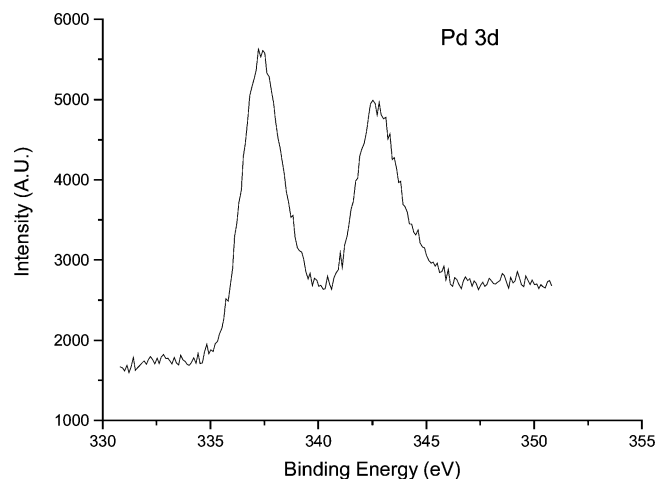


Figure 8. Pd 3d binding energy of Pd species of the Ppy (SDS)/Pd film.

fields at the nitrogen sites, making atoms in their proximity look more positive than others.¹² For the Ppy/Pd film, the spectra of the Pd 3d regions are shown in Figure 8; the 337.3 eV peak appears to dominate the spectrum. This result is interesting because the range of binding energy of Pd(0) species is from 334.9 to 335.5 eV. In our experiment, there is no peak observed in this range, all the Pd species are in cationic nature. In our previous work,¹³ we also observed a small Pd 3d peak of Pd/MoO_x species at higher binding energy (338.0 eV), but the dominating Pd 3d peak still showed the major component is the Pd(0) species. We propose the strong interaction between Pd and Ppy facilitates an easy electron transfer from Pd to Ppy in producing cationic species. This strong interaction may also explain the high electrochemical stability of the Ppy/pd film. The nature of the Pd species of the GC/Pd electrode was also investigated (Figure 9)—we can see the 3d binding energy peaks of Pd exhibit tailing at high binding energy values. This can be due to a higher Pd oxidation state present on the surface, although at low concentrations. Nevertheless, the dominant component of the Pd 3d binding energy is the Pd(0) species.

Dechlorination of 4-Chlorophenol by the ECH Process.

From the introduction, we know both the formation of chemisorbed hydrogen on the metal surface and the interaction of 4-CP with the metal surface forming a metal chloride are important in the ECH process for dechlorination. To study the cyclic voltammetry behavior of the GC/Ppy(SDS)/Pd electrode in the H adsorption/desorption area in the presence of 4-CP,

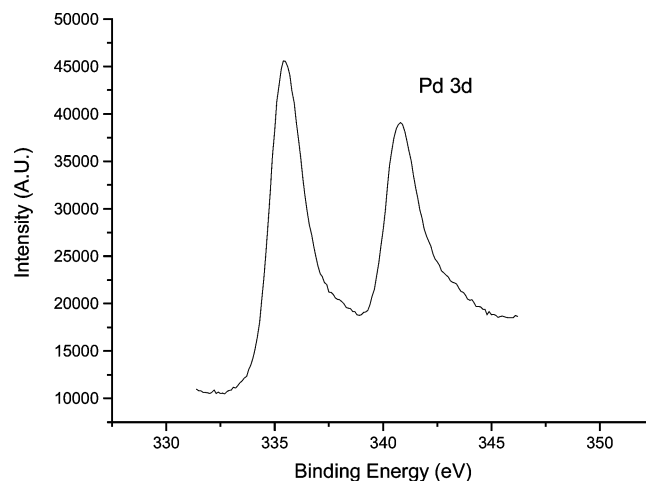


Figure 9. Pd 3d binding energy of Pd species of the GC/Pd film.

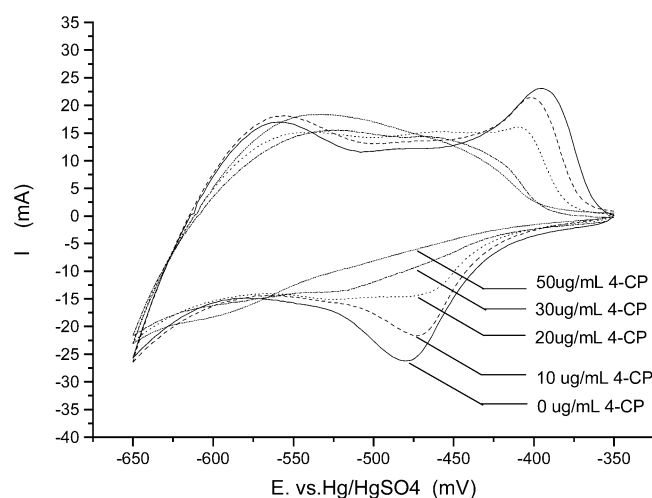


Figure 10. Cyclic voltammograms of the GC/Ppy(SDS)/Pd electrode in 0.5 M H₂SO₄ containing different concentrations of 4-CP, scan rate 20 mV/s.

we observed the change of H adsorption/desorption peaks in the different concentrations of 4-CP. In the experiment, we prepared the 0.05 M H₂SO₄ aqueous solutions containing 0, 10, 20, 30, and 50 ug/mL of 4-chlorophenol as electrolyte, respectively. The GC/Ppy(SDS)/Pd electrode was scanned in the range from -0.65 to -0.35 V in the prepared electrolytes. From -0.35 to -0.57 V, we can see the H adsorption area decreased gradually with the increase of 4-chlorophenol concentration (Figure 10). Also, the H desorption area decreased gradually. From -0.57 to -0.65 V, there is no obvious change in the shape of the CV curve. We suppose the 4-CP molecules occupy some surface position of the Pd atom in place of the H atom in the -0.35 to -0.57 V region. This observation may confirm the dechlorination mechanism (adsorption of 4-chlorophenol at the electrode substrate followed by hydrogenation at the palladium island/electrode) proposed by Cheng.¹ For further investigation of dechlorination of 4-chlorophenol, we studied the current value changes at the GC/Ppy(SDS)/Pd electrode under different potentials, -0.50, -0.55, -0.60, -0.62, -0.64, -0.65, -0.66, -0.67 V, with and without 200 ug/mL 4-CP, by using the constant potential method. We pick the current values at a fairly stable stage (the 300th second) under every potential. In the electrolyte (0.5 M H₂SO₄) without 4-CP, we can see the current values were stable at -0.13 mA from -0.50 to -0.66 V (see Table 1). These currents were believed to be contributed from HER (hydrogen evolution

TABLE 1: The Current Data at the 300th Second under Different Constant Potentials in the Electrolyte of 0.5 M H₂SO₄ with and without 200 μ g/mL of 4-CP

<i>E</i> (V vs Hg/ Hg ₂ SO ₄)	GC/Ppy(SDS)/Pd (mA)		GC/Ppy/Pd (mA)		GC/Pd (mA)		Pd foil (mA)	
	0.5 M H ₂ SO ₄	0.5 M H ₂ SO ₄ + 200 μ g/mL of 4-CP	0.5 M H ₂ SO ₄	0.5 M H ₂ SO ₄ + 200 μ g/mL of 4-CP	0.5 M H ₂ SO ₄	0.5 M H ₂ SO ₄ + 200 μ g/mL of 4-CP	0.5 M H ₂ SO ₄	0.5 M H ₂ SO ₄ + 200 μ g/mL of 4-CP
-0.50	-0.132	-0.871	-0.266	-0.665	-0.454	-0.752	-0.225	-0.166
-0.55	-0.125	-1.014	-0.253	-0.785	-0.457	-0.895	-0.276	-0.233
-0.60	-0.130	-1.152	-0.257	-0.903	-0.449	-0.943	-0.304	-0.293
-0.62	-0.133	-1.275	-0.262	-0.996	-0.451	-1.011	-0.534	-0.427
-0.64	-0.135	-1.396	-0.269	-1.108	-0.487	-1.173	-0.721	-0.521
-0.65	-0.129	-1.525	-0.287	-1.252	-0.536	-1.235	-0.878	-0.648
-0.66	-0.156	-1.873	-0.311	-1.423	-0.587	-1.367	-1.005	-0.865
-0.67	-0.421	-2.053	-0.875	-1.756	-1.123	-1.622	-1.597	-1.326

reaction). And the HER is suppressed because the H atoms formed are absorbed into the Pd particles. The current values were small and stable at the GC/Ppy(SDS)/Pd electrode with the negative shift of potential. When the potential is more negative than -0.66 V, the current increased dramatically. However, the current values at the GC/Ppy(SDS)/Pd electrode increased gradually with the negative shift of potential in the electrolyte (0.5 M H₂SO₄) containing 4-CP and the current values were larger than the current values without 4-CP, respectively. We believe these current values obtained in the electrolyte containing 4-CP are contributed from both the HER current and ECH current. Since the HER currents are fairly stable from -0.50 to -0.66 V in the electrolyte without 4-CP, it is reasonable to suppose the ECH current portion increases with the negative shift of potential in the electrolyte with 4-CP. So we think the Pd-H species is not the sole important factor in the ECH process, the potential is also an important factor. Related observations have been reported by Stock and Bunce⁴ (the influence of constant potential on the dechlorination of atrazine). Since the current values in the electrolyte with 4-CP did not increase dramatically like the current values in the electrolyte without 4-CP when the potential was more negative than -0.66 V, we believe the ECH current portion decreased, i.e., the current efficiency decreased. The same experiment was also applied to the GC/Ppy/Pd electrode, the GC/Pd electrode, and Pd foil (2.0×1.5 cm²). As to the Pd foil, we can see the current increased obviously with the negative shift of the potential in the electrolyte without 4-CP. The explanation can be the Pd foil's relatively weak ability to adsorb hydrogen (there is no obvious hydrogen adsorption current from -0.35 to -0.65 V, see Figure 11)—the HER current increased with the negative shift of potential. In the electrolyte with 4-CP, the current also increased with the negative shift. Interestingly, the current value in the presence of 4-CP was smaller than the current value in the absence of 4-CP. The reason might be that the ECH process did not occur at the surface of the Pd foil because of its poor ability to produce stable Pd-H species. However, the 4-CP molecule still occupied some surface positions of Pd atoms in place of H so that the HER current decreased.

For the bulk electrolysis of 4-CP, a constant current (5mA) electrolysis of 100 mL of the 200 μ g/mL solution of 4-CP was conducted on the GC/Ppy(SDS)/Pd, GC/Ppy/Pd, and GC/Pd electrodes. During the time of 30, 60, 90, 120, 150, and 180 min, samples of electrolysis solution were analyzed and the phenol was the sole product. The result of the dechlorination of 4-CP presented in Figure 12 showed that the dechlorination of 4-CP at the GC/Ppy(SDS)/Pd electrode was more facile than that at the GC/Ppy/Pd electrode and the GC/Pd electrode. Dechlorination efficiencies and current efficiencies for dechlorination reaction followed the electrode sequence GC/Ppy(SDS)/

Pd > GC/Ppy/Pd > GC/Pd. We obtained high current efficiency (49.5%) at the GC/Ppy(SDS)/Pd electrode. In Table 2 the results are summarized. From Figure 12, we can see that the degradation rate of 4-CP decreased with the increase of time at all three electrodes. This result can be explained in terms of decreased adsorption of the 4-CP on the surface of the electrode allowing HER to compete more effectively with ECH. With the decrease of 4-CP in the electrolyte, the rate of electrochemical generation of adsorbed hydrogen becomes faster than the rate at which the

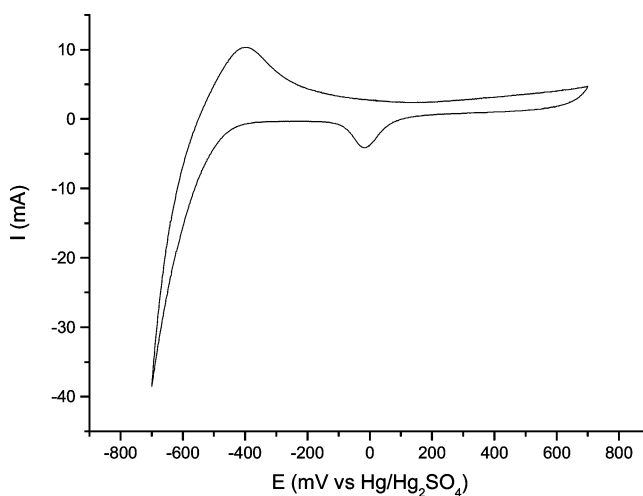
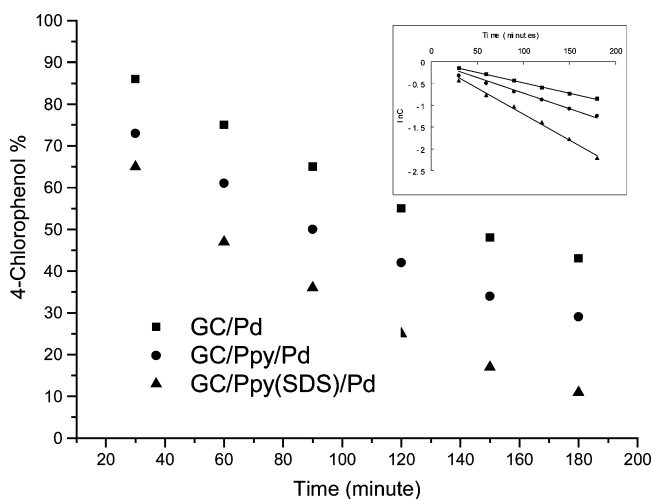
**Figure 11.** Cyclic voltammograms of Pd foil in 0.5 M H₂SO₄, scan rate 50 mV/s.**Figure 12.** Remaining 4-CP with the electrolysis time on three electrodes under galvanostatic condition. Insertion: Logarithmic plot of 4-CP concentration with time—the good linear relationship indicated the loss of 4-CP follows pseudo-first-order kinetics.

TABLE 2: Dechlorination of 4-CP at Different Electrodes (initial 4-CP concentration 200 $\mu\text{g/mL}$)

entry	current (mA)	electrode	time (h)	4-CP remaining (%)	current efficiency (%)
1	5	Pd foil	3	100	0
2	5	GC/Pd	3	43	24.9
3	5	GC/Ppy/Pd	3	29	39.4
4	5	GC/Ppy(SDS)/Pd	3	11	49.5

4-CP can migrate to the surface to be adsorbed and react with H_{ads} . Consequently, a greater proportion of H_{ads} is lost to the unproductive reaction of hydrogen gas evolution. By using a logarithmic plot (the insert in Figure 12) a good linear relationship indicates that the loss of 4-CP follows pseudo-first-order kinetics.

Conclusion

We prepared the polypyrrole/palladium composite film on the glassy carbon electrode by electrodeposition method. The porous structure of polypyrrole film provided more surface areas for depositing Pd particles. The sizes of Pd particles deposited on the porous ppy films were smaller than those of Pd particles deposited on the normal Ppy films. The XPS of Pd 3d spectra demonstrated the Pd species of the Ppy/Pd film are cationic in nature, suggesting strong interaction between the Ppy film and the Pd particles. This modified electrode showed better current efficiency and dechlorination efficiency than the simple Pd film on the electrode. We believe both Pd–H species and potentials play important roles in the dechlorination process. Also, the

strong interaction between the Ppy film and the Pd particles may modify the electronic structure of Pd species, thus affecting their chemisorptive and catalytic properties and enhancing the dechlorination efficiency and current efficiency.

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