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Study on Performance of Electrocatalytic Dechlorination of 2, 5-dichloronitrobenzene by Copper and Palladium Bimetallic Composites Modified Ti Electrode in Aqueous Solution

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In our work, a facile copper and palladium composites modified Ti electrode (Cu-Pd/Ti) was prepared by electrochemical deposition and chemical replacement method, which was applied for electrocatalytic dechlorination of 2, 5-Dichloronitrobenzene (2, 5-DCNB), a typical organic chloride pollutant. The morphologies and structures of Cu-Pd/Ti were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The electrochemical performance was examined by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The experimental results displayed that Cu polyhedrons were formed at the Ti electrode surface (Cu/Ti) and the palladium metals were mainly coated at Cu/Ti electrode in the zero-valent and divalent states. Meanwhile, the copper-palladium composites were uniformly dispersed at the Ti electrode surface. The electrochemical experiments verified that Cu-Pd/Ti composite electrode exhibited high catalytic dechlorination property and large electrochemical active surface area (EASA) owning to the cooperative interaction of Cu and Pd composites materials. The Cu-Pd/Ti displayed better electrocatalytic efficiency towards 2, 5-DCNB reduction than that of the other electrodes in this experiment. With a current density of 2.25 mA/cm^2, the electro-reductive removal rate of 2-DCNB reached 97.1% within 3 hours. The intermediates and mechanisms of dechlorination were identified through high-performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC-MS), and the main final products were properly transformed to aniline. This work may provide a beneficial choice for the effective treatment of DCNBs in the environment.

Keywords: Electrocatalytic dechlorination, Electrochemical degradation, Chloro-nitrobenzene compounds, Cu-Pd bimetallic composites

1. INTRODUCTION

Dichloronitrobenzenes (DCNBs), as a group of widely used intermediates of chemical raw material, are extensively applied in the compounds of herbicides and insecticides in agriculture, wisely used in the synthesis of chemical feedstock, dyes, and the military as explosives [1, 2]. Previous studies have shown that acute toxicity and long-term exposure to dichloronitrobenzene can irritate human eyes, skin, and mucous membranes, which have a severely adverse effect on human beings and the environment [3, 4]. At present, many effective methods have been studied for dealing with chlorinated organic pollutants. These contain physical solutions (especially activated carbon adsorption) [5], advanced oxidative catalysis [6], and biodegradation methods [7]. Among these methods, adsorption is not cost-efficient and further processing is required after treatment, which may create a risk of cross-contamination [8]. The disadvantage of biodegradation is that it may have no tolerance for the toxicity of chlorinated organic compounds [9]. The advanced oxidation method is not only difficult to find suitable catalytic materials but may also produce harmful by-products [10]. Therefore, it is very necessary to find out a new, green, and efficient method to accelerate the reductive dechlorination process of DCNBs, to achieve low toxicity of substance or complete degradation.

Compared with the above-mentioned methods, electrocatalytic dechlorination has been considered as a promising approach for the degradation of organic pollutants because of low cost, mild reaction conditions, easier controllability, and absence of secondary pollutants [11-13]. However, electrochemical dechlorination not only requires sufficient electron donors and reduction potential but also overcomes the influence of hydrogen evolution reaction. It is a very critical step to find the proper catalyst which shows good performance for H_{ads} evolution, moreover, the adsorption capacity of H_{ads} at the catalyst should be appropriate. Cu has already been confirmed that it has good electrochemical properties due to its nature and many advantages, such as good electrical conductivity, stability to fouling in preparative-scale electrolysis [14], and promotion of electrocatalytic reaction [15]. Palladium has a strong ability to adsorb hydrogen and further convert the adsorbed hydrogen into reduced hydrogen [H], so it exhibits excellent activity and selectivity in the dechlorination reaction [16]. To improve the catalytic efficiency of Pd, studies has been carried out by depositing Pd materials on conductive support materials. Herein, it is promising to prepare Pd particles onto the Cu supported materials by a simple method, so that it can not only effectively inhibit the hydrogen evolution reaction, but also more reductive H_{ads} is adsorbed on the electrode surface.

In this work, we report a mild and convenient way for the preparation of Cu–Pd composites modified Ti electrode by electrodeposition and chemical replacement method. This work aims to explore the catalytic properties of Cu–Pd composites for the electrochemical dechlorination reaction. The research results manifested that the dechlorination efficiency of 2,5-DCNB by Cu-Pd/Ti within 3 h was 97.1%, which was obviously higher than that those of Pd/Ti, Cu/Ti, and Ti. This uniform dispersive architecture not only helps to increase the active sites of Cu-Pd catalyst but also improves its hydrogen absorption property by interaction with Cu-Pd bimetallic composites.

2. EXPERIMENTAL

2.1. Chemicals and reagents

2, 5-dichloronitrobenzene (2, 5-DCNB), Cl_4Na_2Pd (36% Pd), and aniline (AN) were bought from Sigma–Aldrich. Sulfuric acid (H_2SO_4, 98%), Sodium chloride (NaCl), Sodium acetate trihydrate ($C_2H_3NaO_2 \cdot 3H_2O$), and Sodium sulfate (Na_2SO_4) were ordered from Sinopharm Chemical Reagent Co., Ltd. Methanol (HPLC grade) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. A titanium (Ti) plate (2 × 2 cm^2, 99.99% purity) were used for preparing bimetallic Cu-Pd/Ti electrodes. All chemicals were used without further processing. Deionized water (DI) was used during the entire experiment.

2.2. Electrode preparation

2.2.1 Pretreatment of Ti electrode

Before each electrochemical deposition, the Ti substrate (2 × 2 cm^2) needs to be pretreated. The pretreatment method was referred to as a reported procedure [17]. Briefly, it was firstly polished by metallographic sandpaper, cleaned in an ultrasonic machine for 20 min, and dried in N_2. And then it was immersed in a mixed solution of HNO_3, HF, and H_2O (volume ratio 4:1:5) for 20 min to remove the oily contaminants. At the last, the titanium plate was sonically washed in acetone, ethanol, and DI for 45 minutes. The pretreated titanium base electrode was stored in ethanol for later use.

2.2.2 Preparation of Cu/Ti

The Cu/Ti was constructed by constant current electroplating. The pre-pretreated Ti electrode was acted as the cathode (that is, working electrode/WE); platinum net electrode (2 × 2 cm^2), and Ag/AgCl (3.0 M KCl) were used as the counter electrode (CE) and the reference electrode (RE), individually. Cu particles were firstly prepared via the electrolysis of 0.04 M $CuSO_4$ solution and 0.5 M H_2SO_4 solution by the CHI760E electrochemical instrumentation, with a current of 62.5 mA/cm^2 for 80 s.

2.2.3 Preparation of Cu-Pd/Ti

Subsequently, the previously prepared Cu/Ti electrode was put into 5 mM Na_2PdCl_4 solution (containing 20 mM sodium chloride solution) for 3 h, where a direct displacement reaction occurred between Pd and Cu [18], and the Cu-Pd/Ti was finally obtained. As a control experiment, the Pd/Ti was electrodeposited by a constant voltage (-0.2 V) for 15 min, where the electrolyte solution was a mixture of 5 mM Na_2PdCl_4 and 0.1 M H_2SO_4.

2.3. Characterizations of the proposed electrodes

2.3.1 Characterizations of morphology and structure

The crystal structures of products obtained at each step were confirmed by the XRD instrument (D/max-2550VB+/PC). The morphologies of the studied samples were studied via the SEM instrument (JSM-7500F) equipped with energy-dispersive X-ray spectroscopy (EDS). The main chemical composition of the samples was obtained by the XPS instrument (Escalab 250Xi).

2.3.2 Physical characterizations

A CHI 760E electrochemical station (Shanghai Chen Hua Instrument Co., China) was applied in the entire electrochemical experiments. The WE, RE, and CE in the system correspond to the study electrode, the counter electrode (Pt plate, 2 × 2 cm^2), and the reference electrode (Ag/AgCl), respectively. All potentials were converted by an Ag/AgCl electrode (3.0M KCl). All experiments were carried out at 25 °C.

The CV and LSV analysis experiments were carried out in a three-electrode system using the CHI760E electrochemical instrumentation. The EASAs of the Cu-Pd/Ti was counted by the following formula [19].

$$\mathrm{EASA}(cm^2) = \frac{Q}{420\mu C/cm^2} \qquad (1)$$

where Q is the charge gained in the CV tests and 420 $\mu C/cm^2$ is the conversion factor.

2.4. Electrocatalytic dechlorination of 2, 5-DCNB

2.4.1 Electrochemical reactor

Dechlorination of 2,5-DCNB was carried out a typical H-type electrolysis room separated by a Nafion 117 membrane. The cathode compartment was equipped with 100 ml of 8 mg/L 2, 5-DCNB (including 0.05 M NaAC background electrolyte), and the anode compartment was equipped with 100 ml of 0.1 M H_2SO_4. In the H-type electrochemical cell, the Cu-Pd/Ti electrodes were used as cathode materials and the platinum mesh electrode was anode. A constant current of 2.25 mA/cm^2 was applied during electrolysis for 3 h with 800 rpm at 25 °C. The effects of dechlorination current densities, different electrodes, and different supporting electrolytes on the dechlorination performance were investigated in 8 mg/L 2, 5-DCNB solution.

2.4.2 The mechanism and composition of analysis for products

The content of Pd and Cu in the material was analyzed through the ICP-OES instrument (Prodigy-ICP, Leeman Labs, USA). Samples were collected every 15 minutes and then analyzed for the rate of degradation of 2,5-DCNB, and its products by HPLC (Thermo scientific Ultimate 3000 high-performance) equipped with a CNW Athena C18-WP column (150 mm×4.6 mm). The mobile phase was a mixture of methanol/water (70/30, v/v), the total flow rate was 1.0 mL/min and the detection wavelength was 254 nm. Each injection volume was 10μL, the column temperature was maintained at 30 °C.

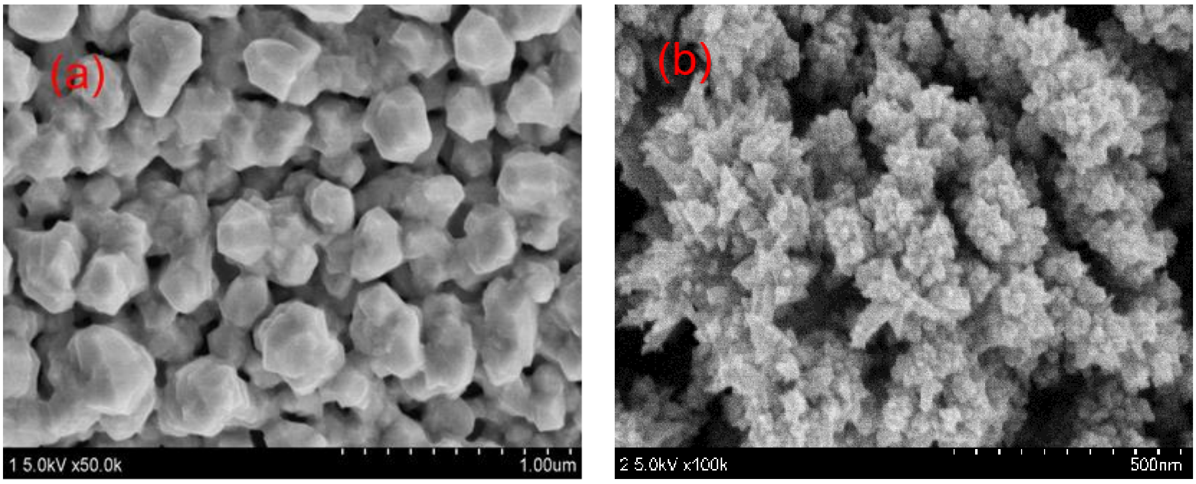
The possible intermediate products of the 2,5-DCNB dechlorination process were detected by GC–MS (Agilent 7890A/5975C). The flow rate of the carrier gas was 1.0 mL/min. The inlet temperature was 250 °C. After the initial temperature was maintained at 40°C for 2 minutes, linearly increased up to 85 °C at 2 °C/min and kept for 1 min, and then increased to 280°C at a temperature of 30°C/min for 5 min. Each injection volume was 1 μL. The temperature of the auxiliary heating zone, ion source, and quadrupole of Mass Spectrometer was set at 250 °C, 230 °C, and 150 °C.

3. RESULTS AND DISCUSSION

3.1. Characterizations of the electrodes

The surface morphologies of the Cu/Ti (a), Pd/Ti (b), and Cu-Pd/Ti (c) were studied by SEM analysis, which is given in Fig. 1, respectively. As shown in Fig.1 (a), the structures of the Cu polyhedron were seen at the Ti electrode surface, which was beneficial to increase the reaction area, and also conducive to the replacement deposition of Pd ions [20]. Fig1 (b) displays that flower-like Pd structures were coated at the Ti electrode surface by electrochemical deposition, but the distribution of Pd structures was not uniform and easy to form clusters. Fig.1 (c) shows that Pd has been successfully wrapped in Cu polyhedrons through the chemical displacement method and substituted at the electrode surface. The uniform dispersion and homogeneous structures of the proposed Cu-Pd composites on the Ti electrode were properly beneficial to the electrocatalytic reaction.

As can be obtained in Figure 1(d), the characteristic peaks of Pd and Cu were displayed on the EDS spectrum of the Cu-Pd/Ti. It indicated that Cu and Pd were indeed deposited at the electrode, which was consistent with SEM results. By the inductively coupled plasma (ICP) test, the concentration ratio of Cu to Pd is about 4:1, which further confirms the existence of Cu and Pd.



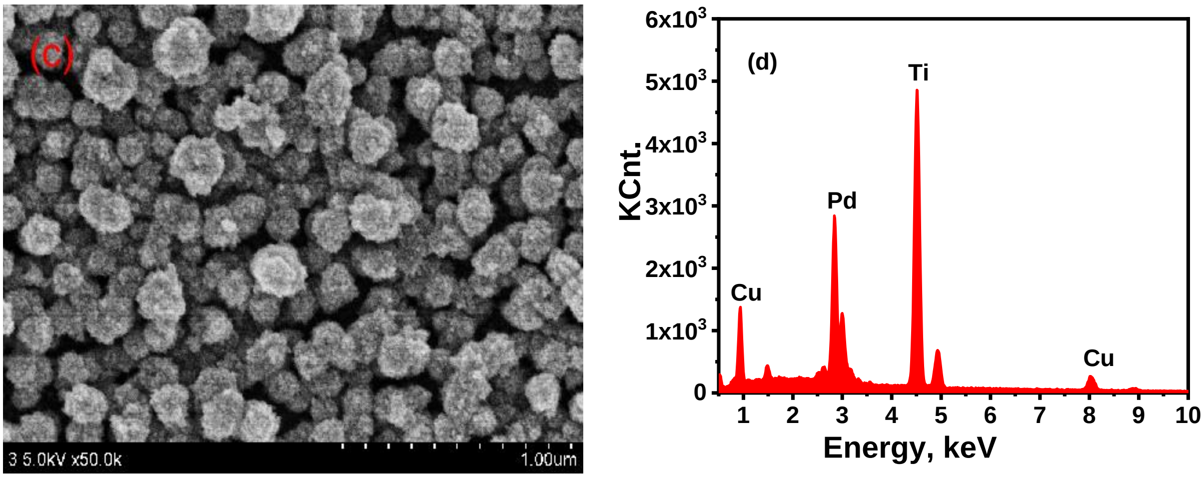


Figure 1. SEM images of different electrodes (a) Cu/Ti; (b) Pd/Ti; (c) Cu-Pd/Ti; (d) EDS spectrum of Cu-Pd/Ti.

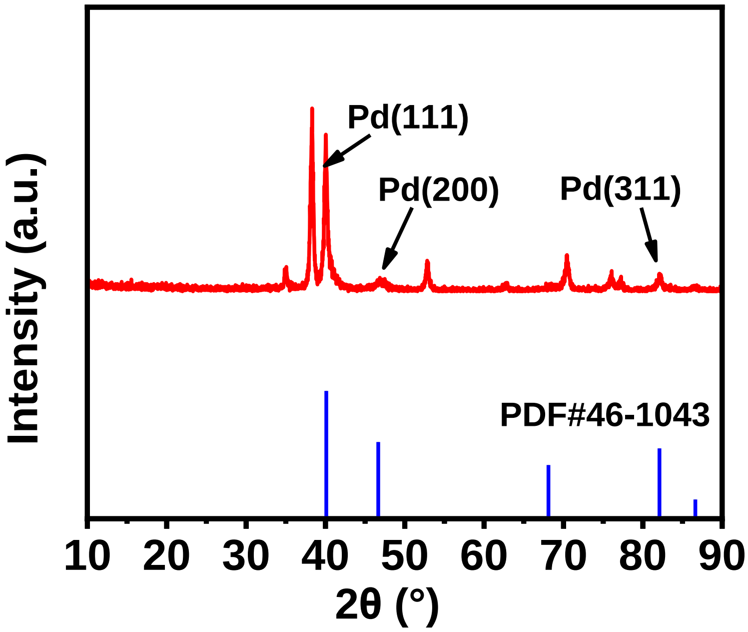


Figure 2. XRD spectrum of Cu-Pd/Ti.

The phase composition and crystallinity of the Cu-Pd/Ti was verified using XRD analysis. The XRD patterns of the Cu-Pd/Ti were shown in Fig. 2 and it exhibited the main characteristic peaks at 40.1°, 46.7°, and 82.1° of Pd (PDF#46-1043), respectively, which corresponded to the face-centered cubic (FCC) lattices of the (111), (200) and (311) facets of the palladium. Obvious diffraction peaks of Pd^0 and Pd^{2+} were observed, indicating that the replacement reaction was successfully achieved.

Due to the weak crystallization and low loading of Cu, its characteristic diffraction peaks were not observed, which also implied that the copper was well dispersed after chemical replacement [21].

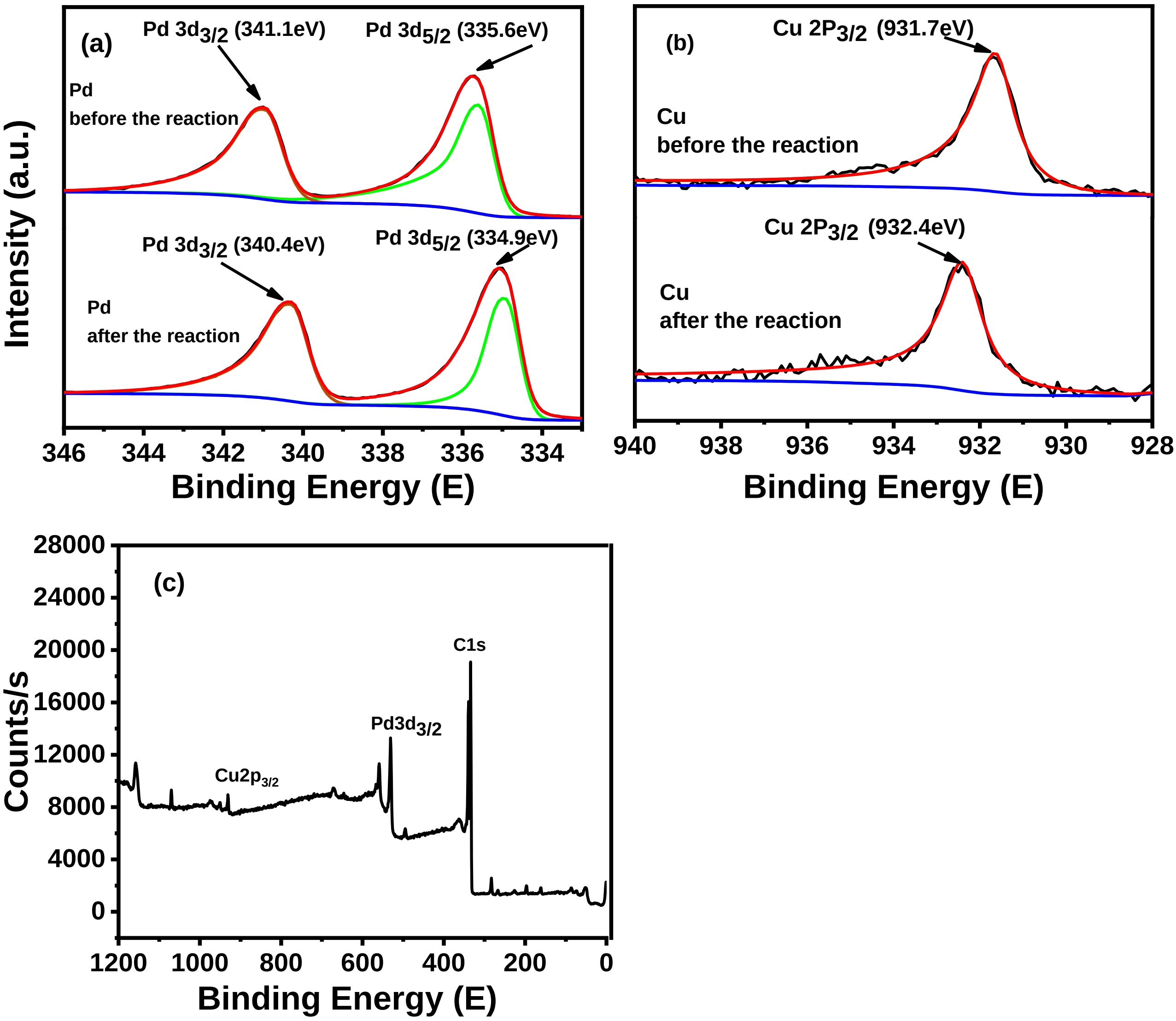


Figure 3. XPS of Cu-Pd/Ti for dechlorination of 2, 5-DCNB: (a) Palladium (b) Copper; (c) Survey scan.

A typical XPS survey spectrum for a Cu-Pd/Ti was displayed in Figure. 3(a), which further indicated the presence of Pd and Cu elements. To confirm the chemical composition and valence states of Pd and Cu, the XPS of Pd 3d and Cu2P were obtained after the 2, 5-DCNB dechlorination reaction. It is observed from the figure that Pd 3d5/2 and Pd 3d3/2 (produced by spin-orbit splitting) appeared at positions 341.1 and 335.6 eV, respectively (Fig. 2c, Pd before). Since the two peaks of Pd 3d5 / 2 and O 1s may overlap, the chemical valence of Pd can be determined by observing whether the two peaks overlap [22]. The shift in BEs confirmed the interaction between the Cu^{2+} and Pd^{2+}. After the addition of Pd, the peak value of Cu 2p3/2 increased from 931.7 eV to 932.4 eV. And the peak value of Pd 3d5/2 decreased from 335.6 eV to 334.9 eV, which indicated that there is an interaction between Cu and Pd.

3.2. Electrochemical analysis

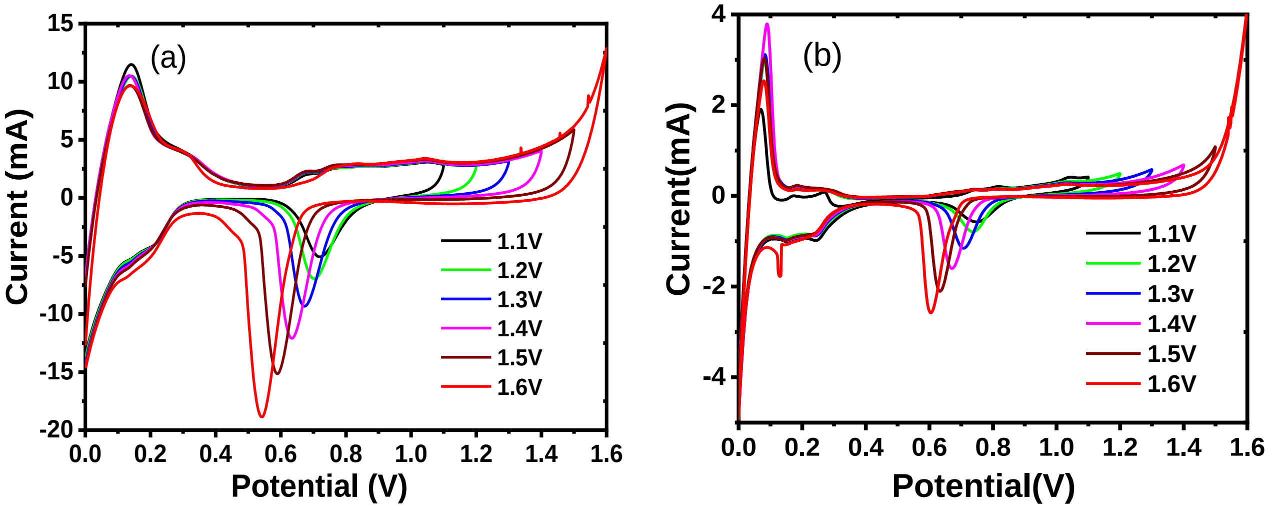


Figure 4. CVs of (a) Cu-Pd/Ti and (b) Pd/Ti for determination of EASAs in N_2-purged 0.1 M $HClO_4$ at 50 mV/s with different upper potential.

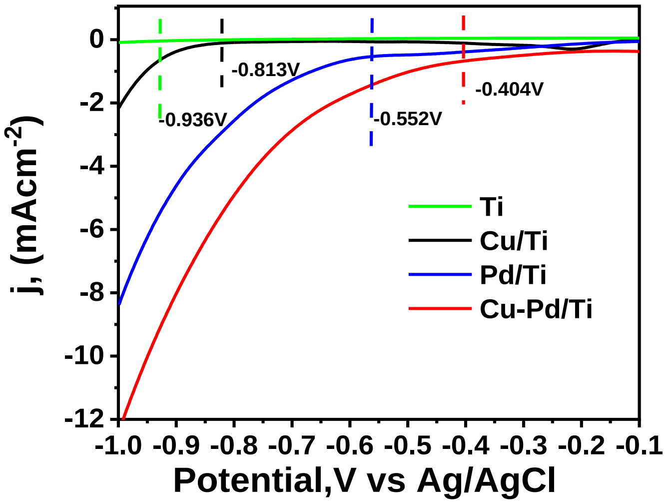


Figure 5. LSV curves of different electrodes in 0.05 M N_2-purged Na_2SO_4 at 50 mV/s.

As described in Fig. 4, the CVs of the Cu-Pd/Ti (a) and Pd/Ti (b) with the voltage limits from 1.1 to 1.6 V. As seen from CVs, with the increase of initial potential, the stripping peak areas of the Pd oxides were gradually increased. Moreover, the stripping currents and peak areas of the Pd oxides at the Cu-Pd/Ti were much larger than those of the Pd/Ti. The calculated charges of Pd/Ti and Cu-Pd/Ti were 7.27 and 12.75 mC, respectively. According to formula (1), the EASAs of the above two electrodes were 17.3 cm^2 and 30.4 cm^2, respectively. The results illustrated that the activity area of Cu-Pd/Ti was enhanced, which proved that the addition of Pd onto Cu/Ti can make the metal Pd more effective through chemical replacement method, and that was possible for a higher electrocatalytic activity for 2, 5-DCNB reduction.

To compare the electrochemical activity of different electrode materials, the LSV measurements of proposed electrodes were performed at the potential ranges of - 0.1 ~ -1.0 V. As can be seen in Fig.5, the hydrogen evolution potentials of each electrode were approximately -0.936 V, -0.813 V, -0.552 V and -0.404 V at Ti (green line), Cu/Ti (black line), Pd/Ti (blue line) and Cu-Pd/Ti (red line), respectively. Compared with other electrodes, the Cu-Pd/Ti showed a larger cathode current and more positive hydrogen evolution potential. The more positive hydrogen evolution voltage can inhibit hydrogen and be conducive to form active atomic H_{ads} for the reduction of organochlorine compounds. The phenomenon can be explained that the good electrical conductivity and large electroactive area of Cu might lead to faster electron transfer inside Pd when Cu was electrodeposited onto the Ti plate. At the same time, the electrons transfer rate further accelerated after Pd was successfully deposited onto the Cu/Ti electrode [23]. This can be demonstrated that the Cu-Pd/Ti showed the highest electrochemical activity for an electro-reductive reaction as compared to the other mentioned electrodes.

3.3. Electrocatalytic dechlorination of 2, 5-DCNB

3.3.1 Effect of different supporting electrolytes

Since the kind and characteristic of supporting electrolytes have an important influence on electrocatalytic reduction, the role of the supporting electrolyte should also be taken into consideration [24].

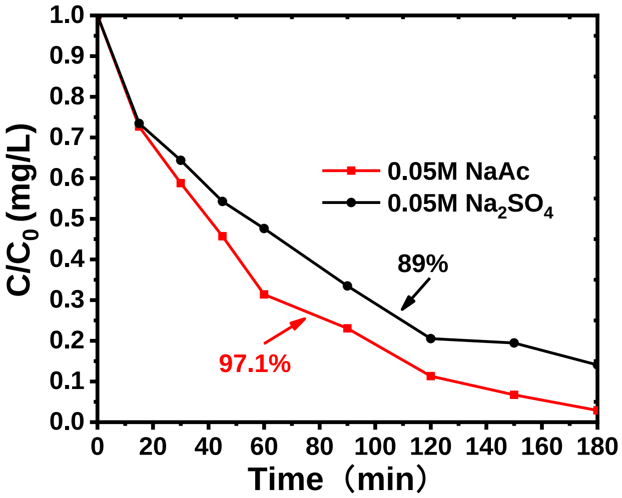


Figure 6. Dechlorination performance of 2, 5-DCNB on the Cu-Pd/Ti in Na_2SO_4 and NaAC supporting electrolyte.

Fig. 6 depicts that the removal rate of 2, 5-DCNB increased from 89% to 97.1%, when the background electrolyte was changed from Na_2SO_4 to NaAC while the other experimental conditions remain unchanged. Previously it has been documented that Cu metal exhibits more satisfactory electrocatalytic activity for polychlorinated molecular structure in the presence of acetic acid [25]. Sodium acetate is a strong soluble electrolyte that is completely ionized in water. In the initial stage of the experiment, there are more free H^+ ions in the anode chamber than in the cathode chamber. After a certain current was added to the cathode, H^+ entered the cathode chamber through the Nafion117 membrane to obtain a HAc/NaAc buffer solution, which had a great infulence in keeping the pH value of cathode electrolyte within an appropriate range [25]. Based on the above discussion, NaAC was chosen as the supporting electrolyte in this experiment.

3.3.2 Effect of current density for electrochemical dechlorination

The current density also played a key role in the dechlorination efficiency for electrochemical reduction of 2, 5-DCNB, directly affecting the productivity of reduced hydrogen, which in turn affects the ECH dechlorination. Dechlorination experiments were conducted at varying currents (0.75, 2.25, 3.75, 7.5, and 11.25 mA/cm^2) in the NaAC supporting electrolyte, and the results are shown in Fig.7.

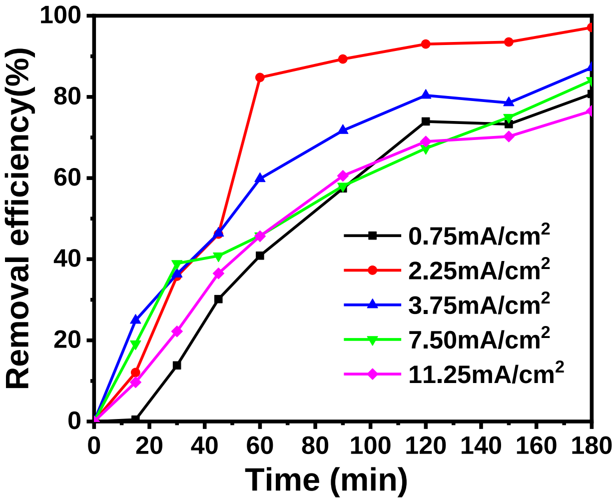


Figure 7. Dechlorination performance of 2, 5-DCNB on the Cu-Pd/Ti with different current densities.

As observed, the removal efficiency of 2, 5-DCNB at the Cu-Pd/Ti electrode increased first and then decreased after dechlorination for 3 h. At a constant current of 2.25 mA/cm^2, removal efficiency reached 97.1% on Cu-Pd/Ti electrode. However, as the current density gradually increases or decreases, the removal efficiency of 2, 5-DCNB is lower than this value. The current density was too low for the dechlorination reaction to produce enough H_{ads}. The higher the current density, the faster the electron transfer rate on the electrode surface, resulting in the output of H_{ads} is too much, and the target pollutants cannot be firmly adsorbed on the electrode surface, that is, the more difficult to suppress the hydrogen evolution reaction. Therefore, the current value of 2.25 mA/cm^2 was the optimum current density for dechlorination based on the removal efficiency.

3.3.3 Electrocatalytic performance for different electrodes

Under the same experimental conditions, the electrocatalytic reduction effects of 2, 5-DCNB were performed at four different electrode materials, and the results could be seen from Fig. 8.

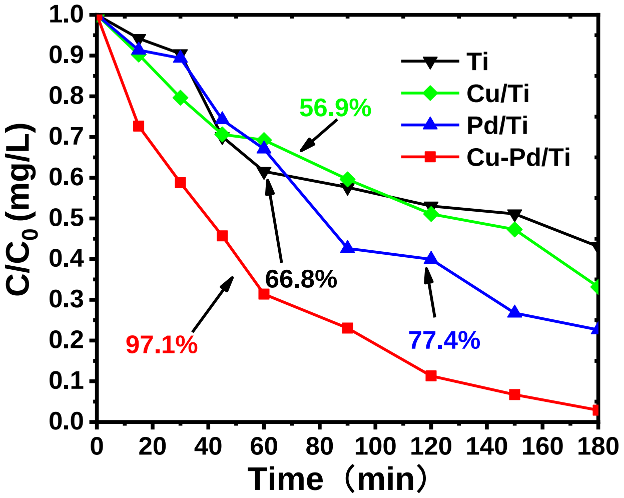


Figure 8. Dechlorination performance of 2, 5-DCNB on the different electrodes. Current density: 2.25 mA/cm^2, catholyte: 8 mg/L 2, 5-DCNB and 50 mM NaAC supporting electrolyte, anolyte: 100 mM H_2SO_4.

After a constant current 2.25 mA/cm^2 was applied to the electrodes, the highest dechlorination efficiency of 2,5-DCNB on Cu-Pd/Ti reached 97.1% (reaction time is 3h), and the dechlorination efficiencies of Pd / Ti, Cu / Ti, and Ti were 77.4%, 66.8%, and 56.9%, separately.

According to the published papers [26, 27], the electrocatalytic hydrogenation technology was considered as a major method to degrade chlorinated organic pollutants. The ECH dechlorination reaction was speculated in Eqs. (1)–(4) at the Cu-Pd/Ti electrode:

$$2\ H_3O^+ \text{ or } 2\ H_2O + 2\ e^- + PdCu \rightarrow 2\ (H_{ads})\ PdCu + 2\ H_2O \text{ or } 2\ OH^- \quad (1)$$

$$R\text{-}Cl + PdCu \rightleftharpoons (R\text{-}Cl)_{ads}\ PdCu \quad (2)$$

$$2\ (H_{ads})\ PdCu + (R\text{-}Cl)_{ads}\ PdCu \rightarrow (R\text{-}H)_{ads}\ PdCu + HCl + PdCu \quad (3)$$

$$(R\text{-}H)_{ads}\ PdCu \rightleftharpoons R\text{-}H + PdCu \quad (4)$$

where R-Cl stands for the reactant. In this work, R-Cl is 2,5-DCNB.

As we can see in the above equations, [H] is firstly generated and can be absorbed on Pd-Cu the surface, then $(R\text{-}Cl)_{ads}$ was replaced by [H], which lead to the dechlorination of DCNBs and the reduction of toxicity. Based on this process, it is a key step to find the metal catalyst which shows good performance in the evolution of H_{ads}, and the adsorption capacity of H_{ads} should be moderate. The existence of Cu(0) particles greatly improved the dispersion state of Pd(0) particles and improved the catalytic activity of electrode materials. The role of Pd (0) is to firmly absorb the generated adsorbed hydrogen, which may be a key factor to improve the dechlorination efficiency of 2,5-DCNB.

We also compared the dechlorination effects of Cu-Pd/Ti or other cathode materials on 2,5-dichloronitrobenzene or other chlorinated organic pollutants in different works of literature. As shown in Table 1, in a comprehensive comparison, the removal efficiency of 2,5-DCNB dechlorination on Cu-Pd/Ti is still satisfactory (up to 97.1%), and the toxicity of pollutants was also reduced to a certain extent. The results showed that the performance of Cu-Pd/Ti was acceptable and promoting, with a certain sense of the potential value of research results.

Table 1. Comparison of electrocatalytic dechlorination effects of chloronitrobenzene pollutants

Catalyst	Target pollutant	Removal efficiency	Reaction time	Notes	Ref.
Cu-Pd/Ti	2,5-DCNB	97.1%	3 h	2.25 mA/cm^2	This work
Pd/Ti	Chloroform	37%	3 h	0.1mA	Ref.[28]
(FeOOH)	p-CNB [a)]	60%	0.5 h	/	Ref.[29]
MES-UASB	2,4-DCNB	78.5 ± 6.1%	120 h	-660 mV	Ref.[30]
$Pd(PPh_3)_4$	2,3-DCNB [b)]	90%	8 h	/	Ref.[31]
IEM-free MECs	2,4-DCNB	91.3%	24 h	/	Ref.[32]
Pd NPs	2,4-DCP [c)]	91.44%	6 h	-0.85V	Ref.[33]
Pd/PPY-SDBS/Ti	2,4-DCP	95%	~2 h	5mA	Ref.[34]
GAC-Fe-Cu	p-CNB	95.3%	2 h	/	Ref.[35]
$Pd/MnO_2/Ni$	2,4-DCBA[d)]	~100%	2 h	1.67 mA/cm^2	Ref.[36]

a) p-CNB:p-chloronitrobenzene; b) 2,3-DCNB: 2,3-dichloronitrobenzene; c) 2,4-DCP:2,4-Dichlorophenol; d) 2,4-DCBA: 2,4-dichlorobenzoic acid.

3.4 The kinetics analysis of 2, 5-DCNB dechlorination

To study the reduction behavior of 2, 5-DCNB on different electrodes, the dynamic analysis was carried out. According to the accurate first-order kinetics reaction conversion of data points, linear fitting, and the fitting of different electrode parameters were summed up in Table 2.

Table 2. The pseudo-first-order kinetics fit results of 2, 5-DCNB

Electrode	k[a)]/min^{-1}	R^2
Ti	0.0044	0.9897
Cu/Ti	0.0056	0.9760
Pd/Ti	0.0088	0.9822
Cu-Pd/Ti	0.0168	0.9919

a) Rate constants on different electrodes; R^2: Coefficient of correlation

As can be inferred from in Fig.S1, the R^2 values of Ti, Cu/Ti, and Pd/Ti electrodes are less than 1, which indicated that the quasi-first-order kinetic reaction model is not consistent. On the contrary, the R^2 values on Cu-Pd/Ti electrodes are close to 1, which is following the quasi first-order dynamic model. As can be seen from the k value of the rate constant, the rate constant of reduction of 2, 5-DCNB on the Cu-Pd/Ti was 0.0168, which was the highest. It also indicated that Cu-Pd composite metal catalyst has higher electrocatalytic activity compared with other electrodes, and speeds up the reduction and dechlorination rate of targeted pollutants.

3.5 Possible pathway analysis of 2, 5-DCNB reduction on Cu-Pd/Ti electrode

The intermediate products and transformation process of 2, 5-DCNB were qualitatively tested in the light of the HPLC and GC-MS, and the results illustrated that the residual dechlorination solution contained few intermediates, which was used to speculate to the possible pathway and mechanism of dechlorination. Fig. S2 and S3 indicated that the peak in the initial sample at 12.63 min represented 2, 5-DCNB, with further dechlorination, the peak gradually decreased. Three major new peaks were observed at 3.92, 7.45, and 9.54 min, which was suspected to be aniline, 5-chloroaniline (5-CAN), and 2, 5-dichloroaniline (2, 5-DCAN) [35, 37-41]. With the increase of reduction time, aniline content was added, but the concentrations of 2, 5-DCAN was gradually reduced. These results were in good accordance with the GC-MS analysis (Fig. S4). Based on the previous experiments performed and the analysis [42-44], it could be hypothesized that a possible pathway was mainly involved for 2, 5-DCNB.

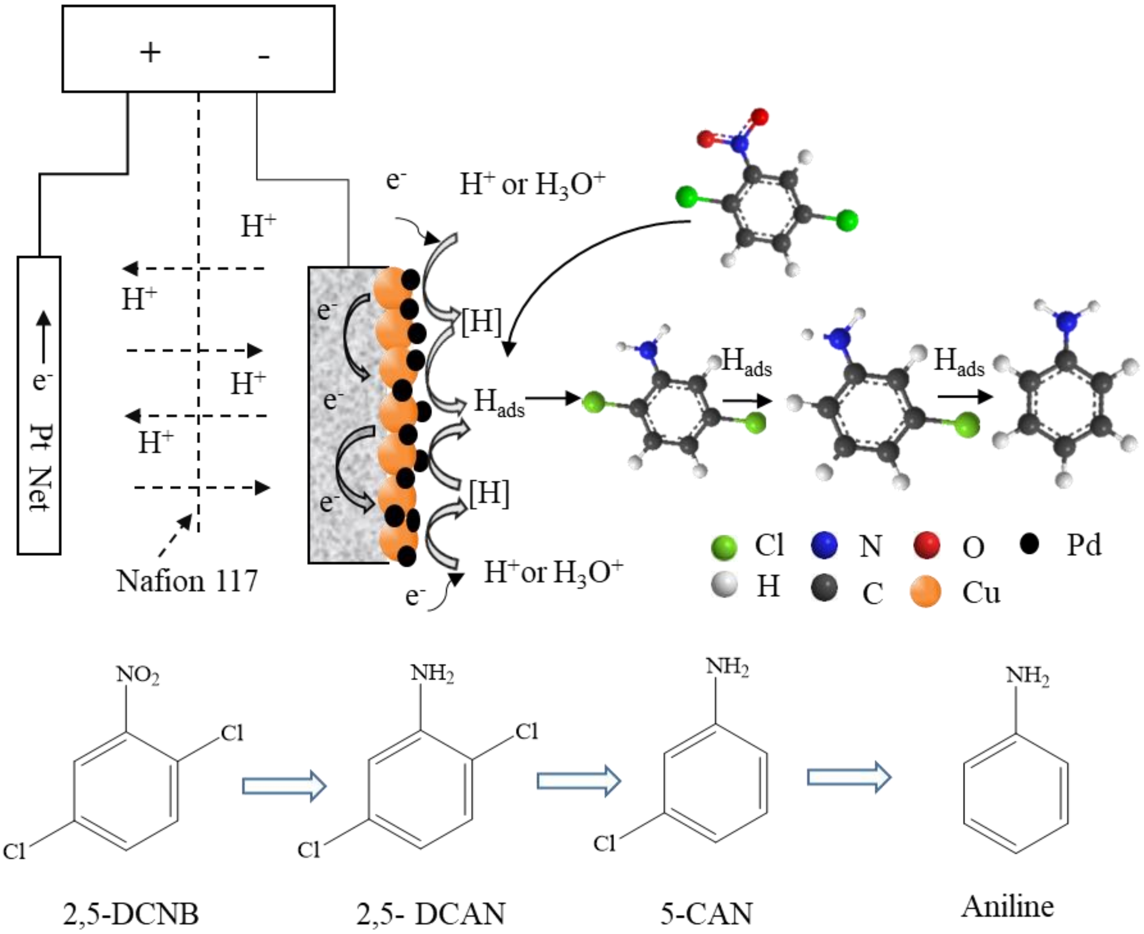


Figure 9. The possible pathway of electrocatalytic dechlorination for 2, 5-DCNB at the Cu-Pd/Ti.

As shown in Figure 9, [H] was mainly produced by electrolysis of H_3O^+ or H^+, and then the active hydrogen atoms [H] were quickly adsorbed on the Cu-Pd/Ti surface. The researchers pointed out that during the dechlorination process, the PdCu-Cl bond was generated on the surface of the catalyst and then was replaced by the reductive [H]. After the C-Cl bond was broken, the product was dissolved in the electrolyte, and the active sites were regenerated on PdCu [45]. According to the mechanisms of electrochemical dechlorination that have been reported in previous studies [46, 47], nitro-compounds were accessibly reduced to amino-substances, and ortho-chlorine was more easily to be removed than para-chlorine. There, it is speculated that 2, 5-DCNB was catalytically transformed to 2, 5-DCAN at first, then dechlorinated to form 5-chloroaniline (5-CAN), and finally converted to form AN.

4. CONCLUSION

In our work, a convenient and environmental-friendly method for the electrocatalytic dechlorination performance of 2, 5-DCNB using a Cu-Pd/Ti electrode was studied. Sodium acetate as a supporting electrolyte and electro-reductive current of 2.25 mA/cm^2 was chosen as the optimal conditions for the electrocatalytic dechlorination. The innovative electrode displayed better catalytic performance than those of Cu/Ti and Pd/Ti for 2, 5-DCNB reduction, which achieved nearly 97.1% of removal efficiency for 2, 5-DCNB dechlorination within 3 h. By analysis of the mechanism, on the one hand, the effective removal of 2, 5-DCNB was achieved, on the other hand, the main product generated was properly aniline, which greatly reduced the toxicity of chlorinated organic compounds without secondary pollutants. This study may provide a basic understanding to develop an environmental-friendly electrocatalytic dechlorination system of 2, 5-DCNB, and an efficient and effective method for the further study of polychlorinated organics.

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SUPPORTING INFORMATION

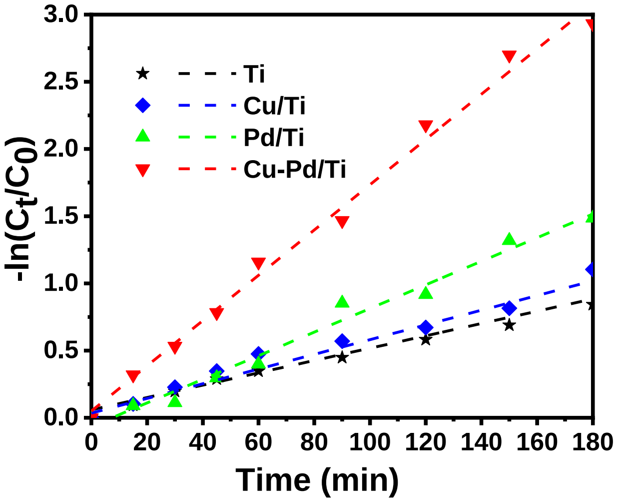


Figure S1 The kinetics analysis of dechlorination at the different electrodes

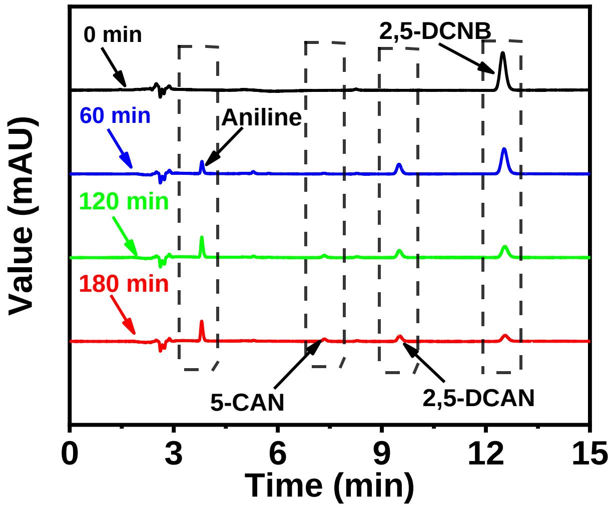


Figure S2 HPLC graphs of the degraded products of 2, 5-DCNB at different times

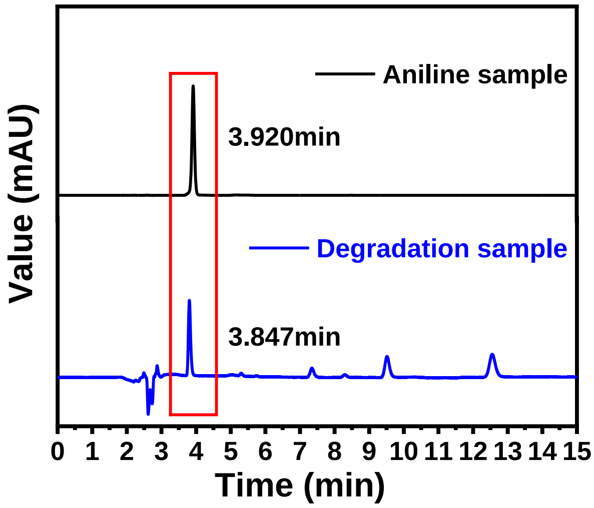
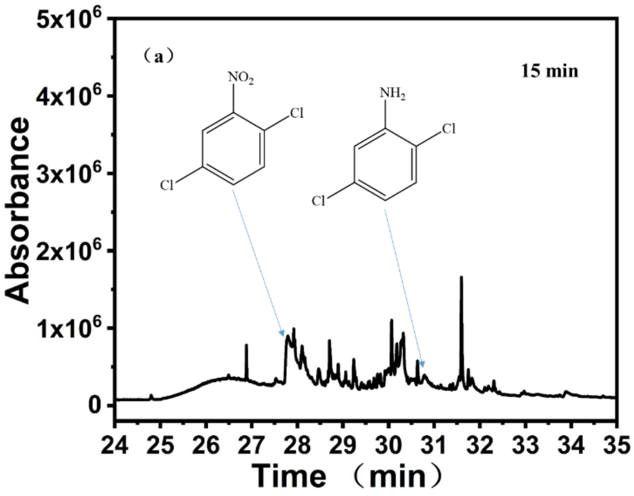


Figure S3 HPLC graphs of the degraded products of 2, 5-DCNB on the Cu-Pd/Ti



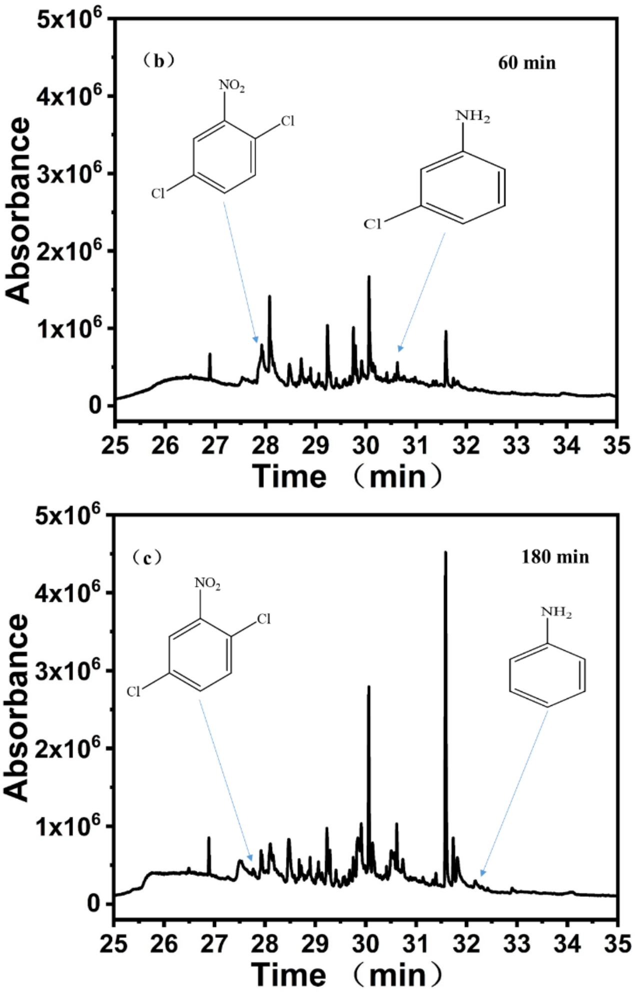


Figure S4 GC-MS chromatography of the products after 2, 5-DCNB dechlorination for (a) 15 min, (b) 60 min, and (c) 180min.

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