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Palladium nanoparticles assembled on titanium nitride for enhanced electrochemical hydrodechlorination of 2,4-dichlorophenol in water

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ABSTRACT

We report a one-pot surfactant-free wet-chemical reduction approach to the synthesis of palladium/titanium nitride (Pd/TiN) and Pd/carbon (Pd/C) composites, in which ~5 nm Pd NPs were uniformly dispersed on TiN or C. In terms of catalytic performance, Pd/TiN showed enhanced efficiency and stability compared with those of Pd/C and bare TiN in the electrocatalytic hydrodechlorination (EHDC) reaction of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. The superior performance of Pd/TiN arises from the promotion effect of TiN. Strong metal-support interactions modified the electronic structure of Pd, which optimized generation of H_{ads}⁺ and 2,4-DCP adsorption/activation. The cathode potential plays a vital role in controlling the EHDC efficiency and the product distribution. A working potential of −0.80 V was shown to be optimal for achieving the highest EHDC efficiency and maximizing conversion of 2,4-DCP to phenol (P). Our studies of the reaction pathway show that EHDC of 2,4-DCP on Pd/TiN proceeded by 2,4-DCP → *p*-chlorophenol (*p*-CP), *o*-chlorophenol (*o*-CP) → P; however, Pd/TiN presented little selectivity for cleavage of *p*-C-Cl vs *o*-C-Cl. This work presents a new approach to enhancing Pd performance towards EHDC through the effects of a support. The strategy demonstrated here could also be extended to design highly efficient catalysts for other hydrogenation reactions.

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1. Introduction

Recently, widespread use of chlorinated phenols (CPs) in pharmaceuticals, agriculture, and the polymer industry has led to severe environmental concerns, with potential to threaten public health [1,2]. However, owing to the high stability of the

Cl–C bonds, these CPs are usually highly resistant to environmental degradation, and also difficult to mineralize by common disposal technologies, such as Fenton/H₂O₂ oxidation, bioprocess, and photocatalytic degradation [3–5]. To detoxify such CPs, one alternative and efficient strategy is to convert them into chlorine-free phenols via a reductive hydrodechlorination

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process, and the resultant phenols can then be completely mineralized through chemical oxidation or biological processes [6,7]. Among current hydrogenation methods [8,9], electrocatalytic hydrodechlorination (EHDC) has received growing attention owing to its high efficiency, mild reaction conditions, no requirements for other chemicals, and low secondary pollution risks [10–12].

In the EHDC process, atomic hydrogen (H^*), a strong reducing agent, is first formed by reduction of H^+ in aqueous solution. The atomic hydrogen then attacks chemically adsorbed CPs on the cathode surface, leading to cleavage of C–Cl bonds and subsequent substitution of Cl by H on the benzene ring. Metallic Pd has been found to be the most effective catalyst towards EHDC, owing to the low overpotential required for H^+ reduction, as well as the appropriate adsorption strength of the Pd– H^* . However, bulk Pd does not have high activity, and its low reserves requires us to reduce the usage of Pd in practical applications [13]. To improve the efficiency of Pd and lower the costs of the electrode, two leading strategies have been established: (1) introducing another cocatalyst, such as transition metals (Fe and Ni) [14,15], graphene [16], and polymers (such as pyrrole-CTAB) [17]; and (2) maximizing the exposure of the Pd sites by shaping the Pd into a nanosized or a porous structure [18,19]. Constructing an active interface between the active metal and the support is another efficient strategy, which is often used to increase the catalytic activity of metals towards certain reactions [20–22]. However, until now, there have been few reports on the effects of supports on tuning the EHDC efficiency of Pd [23,24].

In this work, a surfactant-free wet-chemical reductive approach is developed to synthesize the Pd/titanium nitride (Pd/TiN) and Pd/carbon (Pd/C) composites. Through this approach, Pd NPs in the composite can be controlled to be quite uniform in terms of both size (~5 nm) and shape (spherical), and are also evenly dispersed on the support without any agglomeration. TiN was chosen owing to its good conductivity, chemical stability, and electronic structure. Indeed, Pd/TiN shows considerably enhanced EHDC efficiency and stability compared with those of Pd/C in the EHDC of 2,4-dichlorophenol (2,4-DCP one typical chlorinated phenol). Mechanistic studies have shown that the superior performance of Pd/TiN arises from the promotion effect of TiN. Its strong metal-support interactions with Pd can modify the electronic structure of Pd to optimize H^*_{ads} generation and 2,4-DCP adsorption/activation. We also investigated the cathode potential, which is an important operating parameter in terms of EHDC efficiency and the resulting product distribution. Our results demonstrated that –0.80 V was the optimal working potential to achieve the highest EHDC efficiency and maximum conversion of 2,4-DCP to P. Mechanistic studies showed that the EHDC of 2,4-DCP on Pd/TiN proceeds by 2,4-DCP → *p*-chlorophenol (*p*-CP), *o*-chlorophenol (*o*-CP) → phenol (P); however, Pd/TiN has low selectivity for cleavage of *p*-C–Cl vs *o*-C–Cl.

2. Experimental

2.1. Materials

TiN was obtained from Hefei Kaier Nano Company (China). Before use, it was treated with concentrated HCl for 3.0 h, washed with deionized water until the washings were neutral, and subsequently dried in an oven at 60 °C for 1.0 h. Carbon black (Vulcan XC 72R) was used as an alternative support material (denoted as C below), and purchased from Cabot. $Na_2[PdCl_4]$ and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. $NaBH_4$, HCl, ethanol, 2,4-DCP, *p*-CP, *o*-CP, P, Na_2SO_4 , and chromatography grade methanol were supplied by the Sinopharm Group Chemical Reagent Co., Ltd. China. A 2,4-DCP stock solution was prepared by dissolving 5 g of 2,4-DCP in 1 L of methanol and was stored at 4 °C. Deionized water with a specific conductivity $>18.2 \text{ m}\Omega \text{ cm}^{-1}$ was used throughout the experiments. Carbon paper (Toray 090, with a thickness of 280 μm and a porosity of 0.78) was used as the working electrode substrate.

2.2. Preparation of cathode

The Pd/TiN composite was synthesized as follows: 40 mg of the treated TiN powders was dispersed into 80 mL of deionized water by intense sonication. A 0.8-mL portion of the $Na_2[PdCl_4]$ solution (13.8 mg mL^{-1}) was then dropwise added into the above TiN suspension, and sonicated for a further 30 min. The solution pH was adjusted to approximately 10 by adding a NaOH solution (1.0 mol L^{-1}). Under stirring, an aqueous solution of $NaBH_4$ (8.0 mg mL^{-1}) was slowly dropped into the above mixture over 20 min. After reaction for 1.0 h, a Pd/TiN composite was formed, and the product was collected by adding ethanol and centrifugation (10000 r min^{-1} , 8 min), further washed three times with deionized water and separated by centrifugation (10000 r min^{-1} , 8 min). The final product was dried in 60 °C for 12 h. The same method, substituting TiN with C could lead to the Pd/C composite.

To prepare the working electrode, 15 mg Pd/TiN or Pd/C powders were dispersed in a solvent mixture of 2.5 mL ethanol and 25 μL Nafion by intense sonication to form a catalyst ink. This ink was then transferred onto a carbon paper (area: $2 \text{ cm} \times 2 \text{ cm}$) under an infrared heat lamp, which accelerated the evaporation of liquid and promoted the formation of a uniform film.

2.3. Electrocatalytic hydrodechlorination of 2,4-dichlorophenol in water

EHDC of 2,4-DCP was conducted in a two-compartment electrochemical cell, which was separated by a proton-exchange membrane Nafion-117 to prevent Cl^- flowing into the anode cell to generate Cl_2 . The catalyst-loaded carbon paper served as the working electrode, while an Ag/AgCl wire and Pt foil ($3.0 \text{ mol L}^{-1} \text{ KCl}$, 0.201 V vs SHE at 25 °C) were used as the reference and counter electrode, respectively. The whole cell was immersed in a thermostatic bath to maintain the EHDC reaction at a constant temperature of 25 °C. For each test, 100 mL of N_2 -saturated Na_2SO_4 solution (50 mmol L^{-1}) was added into each compartment, then 1.0 mL of the 2,4-DCP stock solution was added into the cathode compartment to obtain a con-

centration of 50 mg L⁻¹ (0.31 mmol L⁻¹). During the tests, the electrolytes and 2,4-DCP in the cathode compartment were stirred magnetically to form a homogeneous solution. Aliquots (0.5 mL) were taken from the system at certain intervals for composition analysis.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer with Cu K α radiation with a scanning rate of 4° min⁻¹ in the 2 θ range of 20°–80° (Model D/max RA, Rigaku Co., Japan). Scanning electron microscope (SEM) images were collected on Hitachi S-570, Hitachi. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were both obtained on JEOL, JEM-2010, operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was measured with Al K α X-rays ($h\nu = 1486.6$ eV) operated at 150 W on a thermos ESCALAB 250. The Pd loading in the catalyst was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements on an ICP2060t, Tianrui. The concentrations of 2,4-DCP, *p*-CP, *o*-CP, and P were measured by high-performance liquid chromatography (HPLC, Shimadzu 2010-AT) with a UV detector at 280 nm and an ODS-SP column (150 mm $\times$ 4.6 mm). A mixture of methanol and water (volume ratio: 60/40) was used as the mobile phase (1.0 mL min⁻¹). Each sample was pre-filtered with a 0.45- μ m cellulose membrane, and 20 μ L of the filtrate was then injected for analysis.

3. Results and discussion

3.1. Synthesis and characterization of the Pd/TiN composite

Fig. 1 schematically illustrates our surfactant-free wet-chemical reduction approach for the synthesis of Pd/TiN

Fig. 1. Schematic illustration of the Pd/TiN composite synthesis.

composite. In this method, [PdCl₄]²⁻ and commercial TiN powders were first mixed in an aqueous solution, and then NaOH and NaBH₄ were successively added to convert [PdCl₄]²⁻ into Pd particles on TiN. NaOH plays a vital role in the formation of the strong metal-support interactions between Pd particles and TiN. Without NaOH, free Pd particles were found in the solution and the solution remained black after separation of the TiN powders by high-speed centrifugation at 10000 r min⁻¹ for 8 min (Fig. S1 in Supporting Information). It was assumed that the addition of NaOH could precipitate [PdCl₄]²⁻, and promote *in-situ* crystallization of Pd NPs on TiN surface.

Fig. 2(a) presents the XRD pattern of the collected composite, which indicated the presence of a TiN phase (PDF #38-1420) and five strong characteristic diffraction peaks at 2 θ = 36.66°, 42.59°, 61.81°, 74.07°, and 77.96°. No peaks for the Pd phase were detected, likely because of the low content of Pd in the composite (~10 wt%, determined by ICP) and its small size (see below). Fig. 2(b) shows an SEM image of the composite, featuring some granular particles with an approximate size of 20–80 nm, as well as some bright spots with uniform size of only several nanometers (as indicated by the blue arrow). Ow-

Fig. 2. XRD pattern (a) and SEM (b), TEM (c), and HRTEM (d) images of the as-synthesized Pd/TiN composite.

ing to the higher electron density of Pd than that of TiN, these small bright spots likely arise from the Pd phase. Thus, the Pd particles in the composite were nanosized and evenly distributed on the TiN support. Fig. 2(c) shows a TEM image, which further confirmed the diameter of the Pd particles to be approximately 5 nm and well dispersed on the TiN surface. The corresponding HRTEM image in Fig. 2(d) shows a lattice spacing of ~ 0.23 nm for the Pd NP and ~ 0.21 nm for the TiN, matching well with the (111) and (200) atomic planes of Pd (PDF #46-1043) and TiN phase (PDF #38-1420), respectively. These results demonstrate the successful synthesis of a Pd/TiN composite, in which monodisperse ~ 5 nm Pd NPs were well dispersed on a TiN support. Notably, this method could also be extended to prepare Pd/C composites by substituting the TiN with carbon powders under the same conditions. Under these conditions Pd NPs with a size of approximately 5 nm were uniformly dispersed on the carbon support (Fig. S2).

3.2. EHDC performance of the Pd/TiN composite

To evaluate the EHDC performance, the catalyst ink was first prepared and then pasted as a smooth film onto a carbon paper support ($2\text{ cm} \times 2\text{ cm}$), to serve as the working electrode (see Experimental section for procedures). The Pd loading on the electrode was determined to be 1.50 mg by ICP-AES. Controlled potential electrolysis at -0.85 V (vs Ag/AgCl) was then conducted in a N_2 -saturated Na_2SO_4 solution in the presence of 50

mg L^{-1} 2,4-DCP. The ratio of the 2,4-DCP concentration to its initial concentration (denoted as C/C_0) was measured at certain intervals. Fig. 3(a) compares the C/C_0 variation with the electrolysis time when using TiN, Pd/C (Pd content: 10wt%, denoted as Pd/C-10% below), and Pd/TiN (Pd content: 10wt%, denoted as Pd/TiN-10% below) as the catalysts, respectively. These results show that bare TiN is inert; the 2,4-DCP concentration showed little change after 360-min electrolysis. The Pd/C and Pd/TiN were both active; however, Pd/TiN performed better with the 360-min C/C_0 reaching 6.73%, which was much lower than 40.27% of C/Pd. The inertness of TiN and the superior EHDC performance of Pd/TiN to that of C-Pd indicate that the Pd NPs are the only active sites, and TiN has a greater promotion effect on the Pd performance than that of the carbon support. The stability of the Pd/TiN-based cathode was also tested by performing the EHDC at -0.85 V and performing multiple runs. As clearly seen in Fig. 3(b), our Pd/TiN catalyst was highly stable and maintained high efficiency for at least five cycles.

To probe the promotion effect of the TiN, the electronic structures of Pd NPs on TiN and C were qualitatively characterized by XPS measurements. The results in Fig. 3(c) show that both of the XPS spectra in the Pd 3d region exhibited two major peaks located at binding energies of approximately 341 and 343 eV, which could be assigned to $\text{Pd } 3d_{3/2}$ and $\text{Pd } 3d_{5/2}$ of Pd^0 , respectively. This result indicates that Pd NPs in both composites were dominated by the metallic Pd^0 phase. However, the

Fig. 3. (a) EHDC performance of TiN-10%, Pd/C-10% and Pd/TiN under a cathode potential of -0.85 V in a N_2 -saturated 50 mmol min^{-1} Na_2SO_4 solution in the presence of 50 mg L^{-1} of 2,4-DCP; (b) Stability test for Pd/TiN-10%; (c) XPS spectra in the Pd 3d region of Pd/C-10% and Pd/TiN-10%; (d) CVs of the Pd/C-10% and Pd/TiN-10% in a N_2 -saturated 50 mmol min^{-1} Na_2SO_4 solution.

peak positions of Pd 3d_{3/2} and Pd 3d_{5/2} for Pd NPs with the TiN support showed an obvious negative shift of ~0.38 eV compared with those on the C support. This finding suggests that the introduction of TiN increased the Pd electron density. This modification of the electronic structure is usually associated with changes in the catalytic activity of Pd. Fig. 3(d) compares the CV results of Pd/TiN-10% and Pd/C-10% in the potential range of -0.90 to 0.20 V in a N₂-saturated 50 mmol min⁻¹ Na₂SO₄ solution. Both CV cycles featured one oxidation peak at -0.2–0.0 V in the positive scans; however, the peak intensity of Pd/C was much larger than that of Pd/TiN. According to our previous studies [25], this peak should arise from oxidation of H* generated during negative scans from 0.2 to -0.9 V, and then adsorbed on the surfaces of Pd NPs (denoted as H*_{ads}). The amount of this species could be estimated by integrating the charge transferred in this anodic peak and is thus proportional to the peak density. Accordingly, it can be concluded from the CV results that Pd/TiN is less active than Pd/C in the generation of H*_{ads}, and the increased electron density on the Pd NPs induced by TiN is detrimental for H*_{ads} formation. Because H*_{ads} is the only active radical for the 2,4-DCP dechlorination, lower production of H*_{ads} on Pd/TiN-10% should lead to a lower EHDC efficiency than that of Pd/C-10%; however, this is inconsistent with the results in Fig. 3(a).

Considering that the whole EHDC process is an interfacial reaction, adsorption and activation of 2,4-DCP on the catalyst, in addition to H*_{ads} generation, are crucial for the EHDC reaction. Numerous reports have indicated that electron density modifications of metal catalysts can regulate the adsorption/activation behavior of reactants/intermediates onto the metals, in turn affecting the catalytic activity [26,27]. Sun et al. [28] prepared dumbbell-like Pt-Fe₃O₄ nanoparticles, and found that the introduction of Fe₃O₄ could increase the electron density on Pt, which could be used to optimize the adsorption of intermediate oxygenates during the oxygen reduction reaction and improve the Pt activity. Ma et al. [20] also reported that combination of Ir and a CeO₂ support could modify the electron density of Ir and thus change the adsorption behavior of a CO intermediate on Ir, which affected the reaction route and product selectivity for CO₂ reduction. On the basis of these findings, we believe that the electron density modification on Pd NPs could optimize the adsorption of 2,4-DCP over the electrode, and promote mass/electron transfer between H*_{ads} and 2,4-DCP at the electrode/solution interface, leading to superior EHDC performance of Pd/TiN compared with that of Pd/C. Unfortunately, no experimental measurements have quantitatively identified the difference in adsorption behavior of 2,4-DCP over Pd/C and Pd/TiN, and more work on this aspect is currently underway.

3.3. Effects of the cathode potential on the EHDC performance of Pd/TiN

The cathode potential determines the kinetics of water dissociation into H*_{ads} (the sole active species for hydrodechlorination of 2,4-DCP), and a more negative value will usually contribute to rapid generation of H*_{ads}. Accordingly, the cathode

potential is a crucial factor that affects the EHDC performance. Controlled potential electrolysis under a series of potentials from -0.65 to -0.95 V was then conducted in a N₂-saturated Na₂SO₄ solution in the presence of 50 mg L⁻¹ 2,4-DCP, and the ratio of 2,4-DCP concentration at certain intervals to its initial concentration (C/C_0) was also tracked. The results in Fig. 4(a) show that the concentrations of 2,4-DCP all decreased along with electrolysis time, indicating that the EHDC reaction occurs at all the studied potentials. Fig. 4(b) summarizes the potential-dependent EHDC efficiency (calculated as $(1 - C/C_0) \times 100\%$) after the 360-min reaction. This result shows that as the potential decreased from -0.65 to -0.95 V, the EHDC efficiency first increased, reaching a peak of 93.27% at approximately -0.80 V before then decreasing. Thus, -0.80 V was identified as the most effective potential for the cathodic EHDC reaction.

The EHDC kinetics of 2,4-DCP on Pd/TiN-10% under different potentials from -0.65 to -0.95 V were also studied. Fig. 4(c) plots the $-\ln C/C_0$ versus the electrolysis time, clearly showing that the EHDC of 2,4-DCP on Pd/TiN followed a pseudo-first-order reaction under all the studied potentials. The apparent rate constant (k_{ap} , summarized in Table 1) reached a maximum of 0.00719 min⁻¹ under a potential of -0.80 V. Fig. 4(d) presents the relationship between $\ln k_{sp}$ and $\ln E$ (where E is the absolute value of the applied potential), which shows a volcano-like trend of $\ln k_{sp}$ versus $\ln E$. In the potential range from -0.65 to -0.80 V, $\ln k_{sp}$ increased linearly as $\ln E$ increased, while over a more negative potential range from -0.80 to -0.95 V, $\ln k_{sp}$ decreased linearly with $\ln E$. The present findings demonstrate that the EHDC efficiency and kinetics strongly depend on the cathode potential. In the relatively positive potential range from -0.65 to -0.80 V, the EHDC performance could be enhanced by turning down the potential. However, at potentials with a more negative value than -0.80 V, the EHDC efficiency and kinetics declined.

It is well established that, in the EHDC process, the active species H*_{ads} are first generated from proton (or H⁺) reduction at the electrode surface, and subsequently attack and cleave C–Cl bonds of 2,4-DCP to achieve the hydrodechlorination. The kinetics of H*_{ads} generation are controlled by the cathode potential, and a more negative potential will usually accelerate H*_{ads} production, which could provide sufficient H*_{ads} for enhanced EHDC. This effect is likely the main reason for the intensified EHDC reaction under a more negative potential in the range from -0.65 to -0.80 V. However, when the potential is set to be more negative than -0.80 V, the H*_{ads} generation becomes so fast that some species evolve as molecular H₂ via a Heyrovsky or Tafel step [29,30]. As reported in our previous work, the resulting H₂ bubbles may interfere with the mass/electron transfer between the H*_{ads} and 2,4-DCP [25]. Accordingly, we believe that the lower region of EHDC efficiency in the more negative potential range from -0.80 to -0.95 V can be attributed to rapid generation of H*_{ads} under that negative potential, resulting in hydrogen bubbling and a weakened EHDC process.

3.4. EHDC pathway of 2,4-DCP on Pd/TiN

The reaction pathway of 2,4-DCP hydrodechlorination over

Fig. 4. (a) EHDC performance of Pd/TiN-10% under different cathode potentials from -0.65 to -0.95 V in a N_2 -saturated 50 mmol L^{-1} Na_2SO_4 solution in the presence of 50 mg L^{-1} of 2,4-DCP; (b) Dependence of EHDC efficiency on the cathode potential; (c) Pseudo-first-order representation of the EHDC of 2,4-DCP versus time under different cathode potentials; (d) Relationship between the $\ln k_{ap}$ and $\ln E$ (k_{ap} : apparent rate constant; E : the absolute value of the applied potential).

Table 1

Parameters obtained from the pseudo-first-order kinetic model.

Potential / V	-0.65	-0.70	-0.75	-0.80	-0.85	-0.90	-0.95
Apparent rate constant (k_{ap}) / min^{-1}	0.00124	0.00213	0.00482	0.00719	0.00579	0.00232	0.00131
Correlation coefficient (R^2)	0.981	0.990	0.999	0.998	0.989	0.986	0.982

Pd/TiN was investigated by tracking the intermediates by HPLC. It was found that after EHDC at -0.80 V for 360 min, p -CP, o -CP and P could be detected in the electrolyte solution, indicating a reaction pathway of $2,4\text{-DCP} \rightarrow p\text{-CP}$, $o\text{-CP} \rightarrow P$ for EHDC of 2,4-DCP. Fig. 5(a) presents the molar concentration variation of 2,4-DCP, p -CP, o -CP and P, as well as their sum over the reaction time. As 2,4-DCP was consumed, the concentration of P increased rapidly, while those of p -CP and o -CP remained at a very low level (the concentration of o -CP was a little higher than that of p -CP). Thus, hydrogenation of the two C–Cl bonds on 2,4-DCP occurred at nearly the same rate, and the Pd/TiN catalyst showed little selectivity for cleavage of o -C–Cl vs p -C–Cl. The total concentration of the four phenol species was found to be nearly unchanged, indicating that no other mineralization process occurred during EHDC.

Effects of the cathode potential on the product distribution

were also studied, and the molar ratio of 2,4-DCP, p -CP, o -CP, and P along with the electrolysis time under potentials of -0.75 , -0.80 , -0.85 , -0.90 , and -0.95 V were compared in Fig. 5(b). These results showed that at all four potentials, the amount of 2,4-DCP decreased with the electrolysis time, while CP and P increased in concentration. The increase of P was much faster than that of CP, and the concentration of o -CP was lower than that of p -CP. These features indicate that the same EHDC pathway was followed at all the studied potentials. At -0.80 V, the conversion of 2,4-DCP to P was more rapid, confirming that the most efficient EHDC performance occurred at this potential. It should be noted here that the molar ratio of CP during EHDC depended on the cathode potential, and a more negative potential produced a larger amount of CP in solution. Because the EHDC proceeds by $2,4\text{-DCP} \rightarrow p\text{-CP}$, $o\text{-CP} \rightarrow P$, an increased amount of CP in the solution means that more CP detaches

Fig. 5. (a) Intermediate and product analyses during the EHDC of 2,4-DCP under a cathode potential of -0.80 V in N_2 -saturated 50 mmol L^{-1} Na_2SO_4 solution in the presence of 50 mg L^{-1} of 2,4-DCP; (b) Potential-dependent product distribution along with the EHDC of 2,4-DCP.

from the electrode before hydrogenation into P, when the potential shifts to a more negative value. When combined with the fact that the hydrogen evolution reaction was promoted in the potential range from -0.75 to -0.95 V, we conclude that the weakened adsorption of CP on the electrode might arise from the enhanced H_2 bubbling process. Accordingly, to realize complete hydrodechlorination of 2,4-DCP, a moderate potential should be used to balance the H^*_{ads} generation, H_2 bubbling process and 2,4-DCP adsorption.

4. Conclusions

This work reports a simple and surfactant-free wet-chemical reduction approach to the synthesis of a Pd/TiN composite, in which ~ 5 -nm Pd NPs were uniformly dispersed on TiN. Pd/TiN shows considerably enhanced EHDC efficiency and stability compared with those of Pd/C and bare TiN. The superior performance of Pd/TiN arises from the promotion effect of TiN, owing to strong metal-support interactions that modify the electronic structure of Pd for optimized H^*_{ads} generation and 2,4-DCP adsorption/activation. The cathode potential plays an important role in controlling the EHDC efficiency and product distribution. The optimal working potential was -0.80 V for realizing the highest EHDC efficiency and maximized conversion of 2,4-DCP to P. This work presents a systematic investigation of EHDC processes over a novel efficient catalyst, which should advance applications of EHDC technology in real environmental remediation.

References

- [1] M. Czaplicka, *Sci. Total Environ.*, **2004**, 322, 21–39.
- [2] M. B. Alonso, K. A. Maruga, N. G. Dodder, J. Lailson-Brito, A. Azevedo, E. Santos-Neto, J. P. M. Torres, M. Olaf, H. Eunha, *Environ. Sci. Technol.*, **2017**, 51, 1176–1185.
- [3] H. Y. Gao, L. Mao, F. Li, L. N. Xie, C. H. Huang, J. Shao, B. Shao, B. Kalyanaraman, B. Z. Zhu, *Environ. Sci., Technol.*, **2017**, 51, 2934–2943.
- [4] B. Z. Zhu, C. Shen, H. Y. Gao, L. Y. Zhu, J. Shao, L. Mao, *J. Environ. Sci.*, **2017**, doi.org/10.1016/j.jes.2017.06.035.
- [5] G. M. Jiang, X. W. Li, M. N. Lan, T. Shen, X. S. Lv, F. Dong, S. Zhang, *Appl. Catal. B*, **2017**, 205, 532–540.
- [6] J. R. Li, X. H. Li, Y. Ding, P. Wu, *Chin. J. Catal.*, **2015**, 36, 1995–2003.
- [7] D. S. Lee, Y. W. Chen, *Chin. J. Catal.*, **2013**, 34, 2018–2028.
- [8] J. Z. Mao, X. H. Yan, H. Z. Gu, L. C. Jiang, *Chin. J. Catal.*, **2009**, 30, 182–184.
- [9] X. Yu, T. Wu, X. J. Yang, J. Xu, J. Auzam, R. Semiat, Y. F. Han, *J. Hazard. Mater.*, **2016**, 305, 178–189.
- [10] Z. Q. He, K. J. Lin, J. J. Sun, L. N. Wen, C. Gao, J. M. Chen, S. Song, Y. J. Qian, W. P. Liu, *Electrochim. Acta.*, **2013**, 109, 502–511.
- [11] J. J. Li, H. L. Liu, X. W. Cheng, Y. J. Xin, W. X. Xu, Z. P. Ma, J. Ma, N. Q. Ren, Q. Li, *Ind. Eng. Chem. Res.*, **2012**, 51, 15557–15563.
- [12] B. Q. Dong, Y. H. Li, X. M. Ning, H. J. Wang, H. Yu, F. Peng, *Appl. Catal. A*, **2017**, 545, 54–63.
- [13] J. A. Baeza, L. Calvo, J. J. Rodriguez, M. A. Gilarranz, *Chem. Eng. J.*, **2016**, 294, 40–48.
- [14] Y. L. Han, C. J. Liu, J. Horita, W. L. Yan, *Appl. Catal. B*, **2016**, 188, 77–86.
- [15] A. Z. Li, X. Zhao, Y. N. Hou, H. J. Liu, L. Y. Wu, J. H. Qu, *Appl. Catal. B*, **2012**, 112, 628–635.
- [16] A. T. E. Vilian, S. R. Choe, K. Giribabu, S. C. Jang, C. H. Roh, Y. S. Huh, Y. K. Han, *J. Hazard. Mater.*, **2017**, 333, 54–62.
- [17] Z. R. Sun, X. F. Wei, Y. B. Han, S. Tong, X. Hu, *J. Hazard. Mater.*, **2013**, 244–245, 287–294.
- [18] W. J. Li, H. Y. Ma, L. H. Huang, Y. Ding, *Phys. Chem. Chem. Phys.*, **2011**, 13, 5565–5568.
- [19] Y. X. Zhang, X. D. Hao, Z. P. Diao, *Chin. Chem. Lett.*, **2014**, 25, 874–878.
- [20] S. W. Li, Y. Xu, Y. F. Chen, W. Z. Li, L. L. Lin, M. Z. Li, Y. C. Deng, X. P. Wang, B. H. Ge, C. Yang, S. Y. Yao, J. L. Xin, Y. W. Li, X. Liu, D. Ma, *Angew. Chem. Int. Ed.*, **2017**, 56, 10761–10765.
- [21] H. Y. Zhu, Z. L. Wu, D. Su, G. M. Veith, H. F. Lu, P. F. Zhang, S. H. Chai, S. Dai, *J. Am. Chem. Soc.*, **2015**, 137, 10156–10159.
- [22] W. S. Zhu, P. W. Wu, W. S. Zhu, G. S. Foo, Z. L. Wu, X. Gao, G. M. Veith, K. L. Browning, H. N. Lee, M. X. Zhou, B. Liu, H. M. Liu, *Nat. Commun.*, **2017**, 8, 15291, 1–7.
- [23] C. Amorim, X. D. Wang, M. A. Keane, *Chin. J. Catal.*, **2011**, 32, 746–755.
- [24] E. Diaz, A. F. Mohedano, J. A. Casas, C. Shalaby, S. Eser, J. J. Rodriguez, *Appl. Catal. B*, **2016**, 186, 151–156.
- [25] G. M. Jiang, M. N. Lan, Z. Y. Zhang, X. S. Lv, Z. M. Lou, X. H. Xu, F. Dong, S. Zhang, *Environ. Sci. Technol.*, **2017**, 51, 7599–7605.
- [26] G. M. Jiang, H. Y. Zhu, X. Zhang, B. Shen, L. H. S. Zhang, G. Lu, Z. B. Wu, S. H. Sun, *ACS Nano*, **2015**, 9, 11014–11022.
- [27] S. Yang, D. Y. Chung, Y. J. Tak, J. Kim, H. Han, J. S. Yu, A. Soon, Y. E.

Graphical Abstract

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Palladium nanoparticles assembled on titanium nitride for enhanced electrochemical hydrodechlorination of 2,4-dichlorophenol in water

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A palladium nanoparticle/titanium nitride composite (Pd/TiN) was successfully synthesized by a one-pot wet-chemical reduction approach, which showed improved efficiency and stability compared with those of a Pd/carbon composite in electrochemical hydrodechlorination of 2,4-dichlorophenol in water.

Sung, H. Lee, *Appl. Catal. B*, **2015**, 174–175, 35–42.

[28] C. Wang, H. Daimon, S. H. Sun, *Nano Lett.*, **2009**, 9, 1493–1496.

[29] Y. L. Jiao, D. L. Wu, H. Y. Ma, C. C. Qiu, J. T. Zhang, L. M. Ma,

Electrochem. Commun., **2008**, 44, 1474–1477.

[30] Y. Zheng, Y. Jiao, M. Jaroniec, S. Z. Qiao, *Angew. Chem. Int. Ed.*, **2015**, 54, 52–65.

金属钯纳米颗粒/氮化钛复合材料对水中2,4-二氯苯酚的电催化氢化脱氯

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摘要: 随着社会经济的快速发展, 含氯有机物, 特别是含氯苯系物, 在农业、化工和医药等领域的使用量逐年增多, 而使用过程中不合理的排放和控制致使含氯苯系物对生态环境, 特别是水体环境的污染日趋严重。含氯苯系物具有高致毒致癌性, 易生物富集, 且很难被完全降解矿化, 已被国家环保局认定为优先控制污染物。常规的废水处理工艺, 如吸附、氧化及生物降解等, 效率不高, 且具有二次污染风险。电催化氢化脱氯技术是一种新型特别针对废水中含氯有机污染物的处理工艺, 是通过在阴极电解还原水, 原位生成原子态氢, 以进攻苯环上C–Cl键, 通过C–Cl键断裂H原子取代, 使含氯苯系物完全转化为苯系物, 达到去毒去害化的目的, 近年来越来越受到研究者的关注。在整个电催化氢化脱氯技术中, 高效稳定的电催化剂合成是关键, 决定着脱氯效率、脱氯动力学、产物选择性及能量的利用率。

本文报道了一种简易、无需添加任何表面活性剂的湿式还原法制备金属钯/氮化钛(Pd/TiN)和金属钯/碳(Pd/C)复合材料。在该复合材料中, 金属钯颗粒具有均一的纳米尺寸(约5.0 nm)和球状形貌, 且均匀分布在TiN和C载体上。作为针对水体中代表性含氯苯系物2,4-二氯苯酚的电催化氢化脱氯反应催化剂, Pd/TiN所展现的活性和稳定性均优于TiN和Pd/C, 这源于TiN载体的促进作用。当TiN与Pd复合时, 相应形成的Pd–TiN界面可改变Pd表面的电子结构, 进一步优化Pd产活性氢及其吸附活化2,4-二氯苯酚的性能, 因而其催化氢化脱氯活性增加。阴极工作电压是该催化反应中一个重要操作参数, 决定了电催化氢化脱氯的效率和最终产物的构成。实验表明, –0.80 V vs Ag/AgCl是最佳操作电压, 此时2,4-二氯苯酚的电催化氢化脱氯效率最高, 可达到93.27%, 且可实现最大程度的2,4-二氯苯酚向苯酚转化。脱氯反应路径研究发现, 在Pd/TiN催化剂上2,4-二氯苯酚脱氯反应路径为2,4-二氯苯酚→对位一氯苯酚, 邻位一氯苯酚→苯酚, 但Pd/TiN对邻位和对位的C–Cl键断裂基本没有选择性。本文提供了一种新的有效调控Pd材料电催化氢化脱氯性能的方法, 可望用于其他氢化反应体系的高效催化剂的设计合成, 同时可推动电催化氢化脱氯技术在环境污染修复中的应用。

关键词: 氢化反应; 电解; 钯; 氮化钛; 环境修复

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