Thin Solid Films 664 (2018) 27–32

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Preparation of spike-like palladium nanoparticle electrode and its dechlorination properties

Cuishuang Jiang[a], Hongbin Yu[a,*], Ying Lu[a], Suiyi Zhu[a], Zhi Geng[a], Mingxin Huo[a], Xinhong Wang[b,*]

[a] Engineering Lab for Water Pollution Control and Resources Recovery, School of Environment, Northeast Normal University, Changchun 130117, China
[b] College of Resources and Environment, Jilin Agricultural University, Changchun 130118, China

ARTICLE INFO

Keywords:
Polyaniline
Nickel hexacyanoferrate
Carbon nanotubes
Palladium
Dechlorination

ABSTRACT

A composite electrode was prepared by electrodepositing palladium nanoparticles on an interlayer film composed of polyaniline-nickel hexacyanoferrate-carbon nanotubes. Scanning electron microscopy and cyclic voltammetry were employed to systematically characterize and analyze the electrodes. The dechlorination properties were investigated using 4-chlorophenol as a model pollutant and the operating conditions were optimized. The results indicated that the palladium particles presented as spike-like clusters. As compared with the electrode without the interlayer, the composite electrode exhibited a better electrocatalytic activity and stability towards dechlorination because of its higher hydrogen adsorption/desorption charge. The dechlorination efficiency for 4-chlorophenol (100 mg/L) reached to 98.59% in 120 min under the optimum conditions. The corresponding current efficiency was 12.85%, and the predominant product of dechlorination was phenol. The interlayer significantly improved the stability and the performance of the composite electrode although the palladium loading was very low (0.53 mg/cm^{-2}).

1. Introduction

Chlorophenols (CPs), a group of important industrial chemicals, include 19 congeners from monochlorophenol to fully chlorinated pentachlorophenol. Most of them have been identified as carcinogenic, teratogenic and genotoxic chemicals [1–3]. More seriously, these chemicals have been approved to present not only in aquatic ecosystem at concentration level of mg/L [2] but also in human body for the people in North America, Asia and certain European countries at concentration level of μg/L [3,4]. Therefore, eliminating the harm of CPs on the environment has attracted a lot of attention [5].

As far as the detoxification of chloroorganics was concerned, electrocatalytic hydrogenation (ECH) has been confirmed as an effective technique [6–9] due to its rapid rate, mild reaction condition and absence of secondary contaminants [10,11]. In the process of ECH, chemisorbed hydrogen atoms generated by electrolysis of water could attack the CPs molecules, resulting in the addition of hydrogen to π bonds or the reductive cleavage of σ bonds [12,13]. ECH reaction was significantly affected by the catalyst. Palladium has been usually regarded as the most efficient catalyst due to its excellent ability to absorb and adsorb hydrogen [14,15]. However, the pure palladium coating as a cathode endured several shortcomings of high cost and poor stability, which limited its practical application. A Pd particle film with good dispersion and large specific surface area would be beneficial to the ECH process.

In our previous study [16], a conductive polymer of polypyrrole was used to promote Pd dispersion, and the composite electrode exhibited an improved catalytic performance for CPs dechlorination. Polyaniline (PANI) is another conductive polymer that could be used as a host matrix to prepare composite films due to its high conductivity and large specific surface area [17–19]. It was reported that doping electroactive materials in conducting polymer films could usually improve the performance of composite films [17,20]. Nickel hexacyanoferrate (NiHCF) with cyano-bridged structure is a versatile electroactive material [21–24] that could be employed as a proper bed for immobilizing noble metal catalysts [25,26]. As reported in the literatures [9,17–22,27], synergic effects were usually generated between the conductive polymer and the cyano-bridged coordination polymer to improve the performance of composite materials. Therefore, a Pd particle electrode with high electrocatalytic activity for dechlorination might be expected

* Corresponding authors at: Engineering Lab for Water Pollution Control and Resources Recovery, School of Environment, Northeast Normal University, Changchun 130117, China.
E-mail addresses: yuhb108@nenu.edu.cn (H. Yu), www66xh@163.com (X. Wang).

https://doi.org/10.1016/j.tsf.2018.08.031
Received 25 March 2018; Received in revised form 17 August 2018; Accepted 20 August 2018
Available online 23 August 2018
0040-6090/

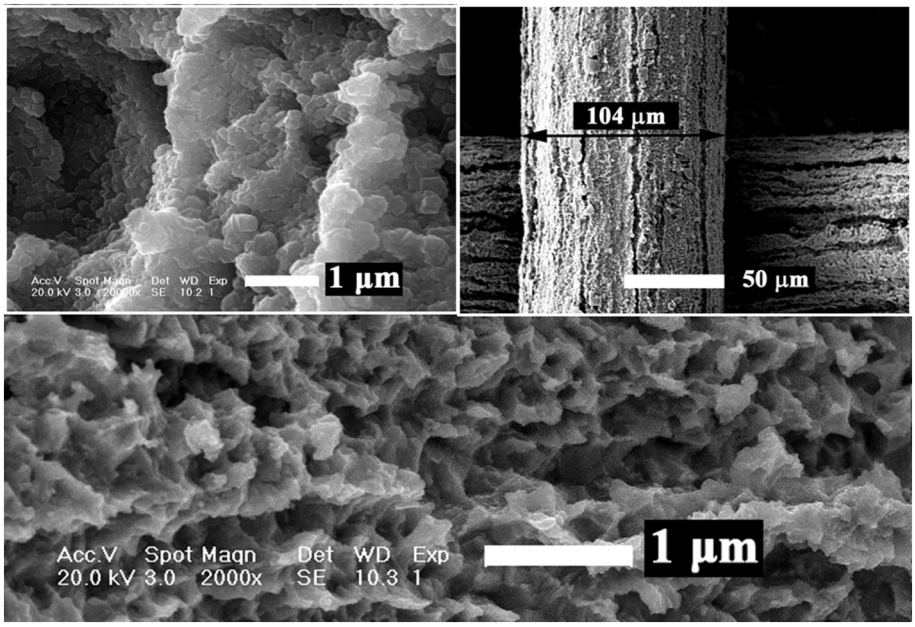

Fig. 1. SEM image of PANI-NiHCF-CNT/Ti films. Insets were the enlarged image (left) and the Ti mesh line covered with this film (right).

if these composite materials were adopted.

In this paper, a Pd particle electrode was prepared through electrodepositing spike-like Pd nanoparticles onto a composite film composed of PANI, NiHCF and carbon nanotubes (PANI-NiHCF-CNT). Scanning electron microscopy (SEM) and cyclic voltammetry (CV) were employed to systematically characterize and analyze the electrodes. 4-CP was chosen as a model pollutant to examine the dechlorination property of the electrodes and the operating conditions were optimized.

2. Experimental

2.1. Materials

The titanium mesh (80 mesh, line diameter 100 μm, purity > 99.5%) used as a substrate was purchased from Baoji Titanium Materials Ltd. (Baoji, China). Multi-walled carbon nanotubes from Beijing DK Nano Technology Co. Ltd. (Beijing, China) would be purified before use. Aniline was purchased from Sinopharm Chemical Reagent Co. Ltd., (Beijing, China) and needed vacuum distillation before use. Other chemicals (Na_2CO_3, $NiSO_4$, $K_3Fe(CN)_6$, H_2SO_4, $H_2C_2O_4$, Na_2SO_4, 4-CP, $PdCl_2$) obtained from Beijing Chemical Works (Beijing, China) were all of analytical reagent grade and used without further purification. Ultra-pure water (18.2 MΩ·cm) was used throughout the experiments.

2.2. Preparation of electrodes

Electrochemical polymerization of PANI-NiHCF-CNT films was similar to the method reported in the literature [19,27] with some modification. In this work, a piece of pretreated titanium mesh [16], a platinum foil and a saturated calomel electrode were selected as the working electrode, the counter electrode and the reference electrode, respectively. The PANI-NiHCF-CNT films were fabricated by using cyclic voltammetry (potential −0.2 − +1.4 V, scan rate 0.05 V/s, 30 cycles) in a mixed solution (100 mL, 0.5 mol/L H_2SO_4, 0.25 mol/L Na_2SO_4, 0.02 mol/L aniline, 0.002 mol/L $NiSO_4$, 0.002 mol/L $K_3Fe(CN)_6$ and 2 mg CNTs). The obtained films were washed with water for several times and dried for use later.

The Pd nanoparticle electrode was prepared by galvanostatic deposition in a two-electrode system with a platinum foil as the anode and the PANI-NiHCF-CNT film or the pretreated titanium mesh as the cathode. The prepared electrodes were named as Pd/PANI-NiHCF-CNT/Ti and Pd/Ti, respectively. The deposition was carried out in 80 mL 1 mmol/L $PdCl_2$ solution at a current density of 4 mA/cm^2 for 40 min until the solution color disappeared.

2.3. Dechlorination

Dechlorination experiments were carried out in a two-compartment unit separated by a proton exchange membrane (Nafion-117, DuPont). The anolyte was 100 mL of 0.1 mol/L Na_2SO_4 solution. The catholyte was 100 mL solution containing 100 mg/L 4-CP and a certain concentration of Na_2SO_4 with different pH values. The Pd/PANI-NiHCF-CNT/Ti or Pd/Ti electrode was selected as the cathode (working area 16 cm^2) for dechlorination at a certain current density for 120 min at room temperature. Magnetic stirring was used in the cathode compartment to facilitate mass transfer.

At given time intervals, 1 mL aliquots were sampled to examine 4-CP and phenol by a high-performance liquid chromatograph (HPLC, Agilent, USA) with a TC-C18 column (150 mm × 4.6 mm). The column temperature was 303 K. The sample volume was 20 μL. The mobile phase was methanol and water (70:30) and its flow rate was 1.0 mL/min. The wave-length of ultraviolet detector was 280 nm.

The current efficiency (CE) was calculated as follows [28]:

$$CE(\%) = nFN_{Phenol} \times 100/It \quad (1)$$

where n is the number of electrons in the reaction (n = 2); F is the Faraday constant (96,500C/mol); N_{Phenol} is the amount of 4-CP consumed (mol); I is the current (A) and t is the dechlorination time (s).

2.4. Characterization

The morphologies of the proposed electrodes were characterized by SEM (JSM-7500F, Japan). The electrochemical characteristics were investigated by CV in a three-electrode system on an electrochemical workstation (CHI650D, China).