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Nitrogen-doped diamond electrode shows high performance for electrochemical reduction of nitrobenzene

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HIGHLIGHTS

- A metal-free nitrogen-doped diamond electrode was synthesized.
- The electrode exhibits high electrocatalytic activity for nitrobenzene reduction.
- The electrode exhibits high selectivity for reduction of nitrobenzene to aniline.
- High energy efficiency was obtained compared with graphite electrode.

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ABSTRACT

Effective electrode materials are critical to electrochemical reduction, which is a promising method to pretreat anti-oxidative and bio-refractory wastewater. Herein, nitrogen-doped diamond (NDD) electrodes that possess superior electrocatalytic properties for reduction were fabricated by microwave-plasma-enhanced chemical vapor deposition technology. Nitrobenzene (NB) was chosen as the probe compound to investigate the material's electro-reduction activity. The effects of potential, electrolyte concentration and pH on NB reduction and aniline (AN) formation efficiencies were studied. NDD exhibited high electrocatalytic activity and selectivity for reduction of NB to AN. The NB removal efficiency and AN formation efficiency were 96.5% and 88.4% under optimal conditions, respectively; these values were 1.13 and 3.38 times higher than those of graphite electrodes. Coulombic efficiencies for NB removal and AN formation were 27.7% and 26.1%, respectively; these values were 4.70 and 16.6 times higher than those of graphite electrodes under identical conditions. LC–MS analysis revealed that the dominant reduction pathway on the NDD electrode was NB to phenylhydroxylamine (PHA) to AN.

1. Introduction

Electrochemical reduction is a promising method to pre-treat wastewater containing anti-oxidative and bio-refractory compounds due to its rapid reaction rate, mild reaction conditions and low apparatus cost [1]. It has been widely used in many fields such as reductive dehalogenation [1,2], reduction of nitrobenzene [3–5], decolorization of azo dyes [6] and reduction of Cr^{6+} [7]. It is well known that the type of cathode material has a crucial effect on electrocatalytic reduction ability. Noble metals such as Pd, Pt, Au and Ag are commonly used as cathode materials [1,6,8,9]. Although these materials have good electrocatalytic activity, their high cost and rarity hinders their use in large-scale applications. On the other hand, graphitic carbon materials and non-noble metals such as Cu, Ni, Fe and Pb often possess low reduction activity and low overpotential for hydrogen evolution, which results in water splitting and decreases coulombic efficiency. Therefore, a cost-effective cathode material with high electro-reduction activity is highly sought after.

As an important metal-free electrode material, doped diamond electrodes exhibit superior electrochemical properties unlike other carbon allotropes. They possess a wide potential window, high resistance to surface adsorption and superior electrochemical and mechanical stabilities [10–14]. After doping, the conductivity of diamond is greatly enhanced. The electrochemical properties of doped diamond can also be tuned by varying its chemical composition [15]. More importantly, nitrogen-doped diamond (NDD) exhibits more negative hydrogen evolution potential than most other reported cathode materials [3,16]. This property indicates that most types of contaminants can be reduced in the potential range without obvious hydrogen evolution, which results in high energy efficiency. In addition, N-doping can generate positive charges in neighboring carbon atoms because the high electronegativity of N polarizes the adjacent carbon atoms; this feature may be favorable for electron transfer. These properties suggest that nitrogen-doped diamond (NDD) electrode may be an ideal electrode material for electrochemical reduction.

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Nitrobenzene (NB) is widely used in various chemical processes to produce dyes, pharmaceuticals, aniline and explosives. It is frequently released into the environment from the effluent of chemical plants. As a hypertoxic compound that is a suspected carcinogen, NB has been listed as a priority pollutant by the United States Environmental Protection Agency. It is necessary to remove NB when it exists as a pollutant. The biodegradation of nitrobenzene proceeds with difficulty because the electrophilic nitryl decreases the electron density of the benzene ring [17] and the toxicity usually inhibits the microbial activity. Although NB can be oxidized by the very powerful oxidizing agent $^{\bullet}$OH [18], most of these processes are energy- and cost-intensive. Conversely, the reduction of NB to aniline (AN) is more efficient, and AN can more easily undergo mineralization than NB through microbiological or chemical approaches [17,19,20]. Moreover, the toxicity of AN is lower than that of NB according to acute toxicity and mutagenicity tests [17,21]. Therefore, the reductive transformation of NB to AN is a feasible method for cost-effective treatment of certain wastewaters.

In this study, we developed a metal-free electrode material based on NDD and evaluated its electrocatalytic activity through NB reduction. The effects of cathode potential, electrolyte concentration and pH on NB reduction were investigated. The electrocatalytic performance of NDD for NB reduction is discussed in terms of NB reduction efficiency, AN formation efficiency and coulombic efficiency (CE, %). For comparison, NB reduction was also performed on a graphite electrode. Finally, the reductive pathway of NB to AN at the NDD electrode is discussed.

2. Experimental

2.1. Preparation of NDD electrode

NDD was grown on a pretreated titanium sheet by microwave-plasma-enhanced chemical vapor deposition. To aid the nucleation and growth processes, the substrate was ultrasonically pre-treated in a diamond suspension with acetone as the solvent before deposition. The growth parameters were as follows: pressure = 5.7 kPa, temperature = 460 °C and deposition time = 10 h. The gas flow rates were maintained at 90, 1.5 and 1 sccm (standard cubic centimeter per minute) for H_2, CH_4 and N_2, respectively.

2.2. Characterization

The morphology of the NDD film was characterized using a scanning electron microscope (SEM, Hitachi S-4800). The crystal structure was obtained using an X-ray diffractometer (XRD, Shimadzu LabX XRD-6000) equipped with Cu Kα radiation. The Raman spectrum was recorded via a Renishaw Micro-Raman system 2000 spectrometer, which was operated with He–Ne laser excitation (wavelength = 632.8 nm). The chemical state and composition of NDD were studied by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250).

2.3. Electrochemical experiments

A double-chamber cell where the chambers were divided by a cationic exchange membrane (Nafion 117) was employed for the electrochemical experiments. The size of each compartment was 25 mm × 20 mm × 50 mm. All the electrochemical experiments were performed using an electrochemical workstation (CHI 660D) with the conventional three-electrode system: a NDD electrode as the working electrode, a platinum electrode as the auxiliary electrode and a Ag/AgCl electrode as the reference electrode. The distance between working electrode and auxiliary electrode was 18 mm. The cathode chamber contained 10 mL of 100 mg L^{-1} NB with sodium sulfate as the electrolyte while the anode chamber only contained electrolyte. The effective electrode area was 20 mm × 20 mm. The solution was well mixed using a magnetic stir bar.

Cyclic voltammetry (CV) was performed using 0.07 M Na_2SO_4 solution with and without NB. The solution was purged with nitrogen gas for 10 min to drive away the dissolved oxygen. The scanning rate was set as 10 mV s^{-1}.

2.4. Analytical methods

The concentrations of NB and AN were measured using a high performance liquid chromatograph (HPLC, Waters 2695) equipped with a C18 column (15 cm × 4.6 mm × 5 μm) and a UV detector (254 nm) at a column temperature of 30 °C. The mobile phase was methanol/water 60:40 (v/v) with a flow rate of 1 mL min^{-1}. To identify intermediates of the NB reduction reaction, accurate-mass TOF LC–MS (Agilent 6224) equipped with an electrospray ionization source was applied. A solution of methanol/water 50:50 (v/v) with a flow rate of 0.2 mL min^{-1} (100 mm × 3 mm × 1.8 μm Agilent ZORBAX SB-C18 column) was used as the mobile phase. The mass spectrum was recorded in the positive ion mode between $m/z = 50$ and 500.

The NB removal efficiency was calculated as follows:

$$\text{NB removal efficiency} = \frac{C_{\text{NB}0} - C_{\text{NB}t}}{C_{\text{NB}0}} \times 100\% \qquad (1)$$

where $C_{\text{NB}0}$ is the initial NB concentration (mM) and $C_{\text{NB}t}$ is the NB concentration at electrolysis time t (mM).

The AN formation efficiency was calculated as follows:

$$\text{AN formation efficiency} = \frac{C_{\text{AN}t}}{C_{\text{AN}0}} \times 100\% \qquad (2)$$

where $C_{\text{AN}t}$ is the determined AN concentration at electrolysis time t (mM). $C_{\text{AN}0}$ is the theoretical concentration of AN that can be converted from the total quantity of NB assuming a conversion rate of 100% (mM).

The CE for AN formation was estimated as follows:

$$\text{CE for AN formation} = \frac{n \cdot C_{\text{AN}t} \cdot V \cdot F \cdot 10^{-3}}{Q} \times 100\% \qquad (3)$$

where $n = 6$, the theoretical transferred electron number for reduction of NB to AN; V is the volume of the total cathodic electrolyte (L); F is Faraday's constant (96,485 C mol^{-1}); and Q is the total electric charge recorded during the process of the reaction (C).

The CE for NB removal was calculated as:

$$\text{CE for NB removal} = \frac{n \cdot (C_{\text{NB}0} - C_{\text{NB}t}) \cdot V \cdot F \cdot 10^{-3}}{Q} \times 100\% \qquad (4)$$

3. Results and discussion

3.1. Characterization of NDD electrode

The surface morphology of the NDD film was characterized by SEM. As shown in Fig. 1a, the film appears to be continuous and uniform over the whole Ti sheet without any obvious cracks, and the particle size of the diamond crystallites ranges from 0.5 to 1.5 μm. The Raman spectrum of NDD (Fig. 1b) shows distinct peaks at approximately 1327 cm^{-1} and 1587 cm^{-1}, which correspond to the formation of diamond with sp^3 bonds and amorphous or graphitic carbon with sp^2 bonds, respectively. The peak intensity ratio of sp^2/sp^3 was calculated to be 0.41. The film appears to possess a high content of sp^3-bonded diamond structure because the cross-sectional scattering coefficient for graphite is approximately 50 times greater than that for diamond [22]. The formation