Development and reaction mechanism of efficient nano titanium electrode: Reconstructed nanostructure and enhanced nitrate removal efficiency

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ABSTRACT

In this study, an efficient nano titanium electrode (ENTE, treated electrode) was fabricated for electroreduction of nitrate in groundwater. The nano titanium electrode showed a regular reticulate nanostructure by scanning electron microscopy. An acid environment and electrochemical treatment of the nano titanium electrode (NTE, untreated electrode) induced ruptures into its regular nanostructure, which led to improved nitrate electroreduction efficiency. X-ray photoelectron spectra revealed titanium dioxide in the anatase phase at the electrode surface and the treatment did not affect the composition or crystal form. The electroreduction activity of the treated electrode (94.6%) was almost twice as high as that of the untreated electrode (65.8%). In the presence of NaCl, by-products that formed during electroreduction, particularly ammonia, were removed by hypochlorite ions. The optimum NaCl concentration in the electrochemical system was determined as 1.5 g/L, which led to a low level of ammonia formation (<1.0%) and an overall efficiency total nitrogen removal of 92.6%.

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1. Introduction

Titanium dioxide nanotubes have attracted considerable interest owing to their high chemical stability [1], formation of unique tubular nanostructures [2], low cost, good environmental safety [3], and ion-exchange ability [4]. Recently, titanium dioxide nanotubes have been extensively studied for a wide range of applications including photocatalysis [5], energy storage devices [6], solar cells [7], sensors [8], and supercapacitor electrodes [9,10]. Nanostructured titanium dioxide nanotubes exhibit excellent photocatalytic activity towards removal of paraquat [1], methyl orange [11] and acetaminophen [12]. Nitrates have the potential to form nitrosamines [13], which have become a widespread environmental problem in water resources. Nitrosamines have been linked to many diseases in humans, such as cancer and methemoglobin, and there is a need for methods to effectively remove these compounds [13]. Many efforts have been devoted to synthesizing cathodes for nitrate reduction. Metal and metal alloys such as Cu [14], Fe, Ti and Cu/Zn [15] are commonly used cathodes for the electroreduction of nitrate. However, these electrodes typically result in low nitrate removal efficiencies. The cathode material and surface structure control the efficiency of electroreduction systems, which has motivated research into materials with improved electrochemistry properties [16–18]. Previous studies have focused on specific coatings or modified (Ni, Cu, Pt, B, Rh, Pb) and nanostructured electrodes [19–23]. For instance, Reyter et al. [24] studied a cathode formed by co-electrodeposition of Pd and Cu, which showed high nitrogen selectivity during nitrate removal, although the overall nitrate reduction efficiency of the electrode remained low. There remains a need for cathodes that have high nitrate removal efficiency. Wang et al. [19] synthesized a Ti nano electrode with a large specific surface area using an electrochemical anodization method. The preparation conditions were optimized, based on study of the response surface methodology, to achieve a nitrate reduction efficiency around 125%–144% higher than that of the untreated electrode. However, the reduction efficiency of the nano electrode in the study of Wang et al. [19] remained too low for practical applications. Much work remains to be done for improving the performance of the nano electrodes.

The real surface area and electric double layer of nano electrodes play important roles in their electrochemistry. The real surface area of electrodes having different roughness can be conveniently measured by chronoamperograms [20]. In the study of Zhang et al. [20], a higher real electrode surface area resulted in greater contact of electrolyte with the electrode surface and a shorter proton diffusion distance, which improved the electrode performance. Therefore, the aim of this study was to create nano electrodes with high real surface areas in order to influence the electric double layer formed during electrolysis and improve nitrate electroreduction performance. The length of titanium dioxide nanotubes is strongly affected by their preparation conditions. Marien et al. [1] investigated the influence of nanotube length on the photocatalytic degradation of paraquat and found that short

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tubes with a small internal diameter, which formed under shorter anodizing times, showed poor photocatalytic activity, due to repressed pollutant diffusion processes [1]. Conversely, long tubes with thin walls, which formed at longer anodizing times provided longer distance for light absorption and pollutants diffusion to obtain oxidizing species from the electron-hole pairs [1]. Preparation conditions can control the electrode nanostructure and titanium dioxide nanomaterials having various structures have been formed using methods, such as hydrothermal treatments [4], microwave methods [25] and electrochemical anodization [26]. Among these methods, electrochemical anodization is attractive because of its low cost and ease of operation. Thus, in this study, nano electrodes were prepared using electrochemical anodization. Subsequently, oxidations were performed on the as-prepared nanostructured titanium electrodes at low currents to reconstruct their nanoporous structure. These features of the treated electrodes also affected the formation of the electric double layer during electrolysis which played a key role in electron transport [20].

Electrode size has implications for their practical applications. Zhang et al. [20] prepared a Ni-B/NPC electrode using a 4×5 mm^2 Cu foil substrate, which demonstrated improved mass transfer and increased surface adsorption. Sun. et al. [27] fabricated titanium dioxide nanotube array electrodes on 10×10 mm^2 titanium sheets, which incorporated substoichiometric titanium oxides to enhance the kinetics of ion and electron transport at the electrode. Roman et al. [28] studied the preparation and characterization of titanium dioxide nanotube films on 10×10 mm^2 titanium plates. Tian et al. [29] investigated the preparation of titanium dioxide nanotubes by anodic oxidation and optimized the preparation process parameters on 15×25 mm^2 titanium plates. Electrodes for use in practical applications will always require larger sizes than those used in experiments. Thus, accurate techniques and preparation methods are required for scale up to large area electrodes for use in practical applications. In this study, a substrate of pure titanium with an area of 100×25 mm^2 was used, which is an order of magnitude larger than substrates used in previous reports [20,27–29]. Thus, the electrodes prepared in this study have sizes that are more relevant to potential practical applications.

In this study, nano titanium electrodes with a high specific surface area were fabricated by an electrochemical anodization method to grow titanium dioxide nanotubes over the surface. Efficient nano titanium electrodes were obtained by the oxidation of the as-prepared electrodes under a low-level current, which further altered the nanostructure. Scanning electron microscope and X-ray photoelectron spectroscopy studies revealed the surface morphology and crystalline form of the electrode, and provided insight into the formation mechanism. The electrochemical activity of the as-prepared electrodes towards nitrate reduction was investigated in nitrate solution. In addition, harmless disposal of nitrate-containing wastewater was studied by controlling the introduction of NaCl into the electrochemical system.

2. Materials and methods

2.1. Chemicals and materials

Using acetic acid (CH$_3$COOH, ≥99.5%), hydrofluoric acid (HF, ≥40.0%) to the synthesis of nanostructure layer on the titanium substrate. Commercially graphite (100 mm × 25 mm) and pure titanium with dimension of 100 mm × 25 mm to the synthesis of nano titanium electrodes. Sulfuric acid (H$_2$SO$_4$, GR, 95.0%–98.0%), graphite electrode (100 mm × 25 mm) and NTEs was used to form efficient nano titanium electrodes. The platinum (Pt, TohoTech Company, Japan) electrode with dimension of 100 mm × 25 mm, sodium nitrate (NaNO$_3$, ≥99.0%), sodium sulfate (Na$_2$SO$_4$, AR), sodium chloride (NaCl, ≥99.5%), hydrochloric acid (HCl, GR, ≥99.5%), sulfanic acid (H$_3$NO$_3$S, ≥99.5%), potassium sodium tartrate (KNaC$_4$H$_4$O$_6$·4H$_2$O, ≥99.0%), Nessler reagent prepared by sodium hydroxide (NaOH, ≥96.0%), potassium iodide (KI, ≥99.0%) and

mercuric iodide (HgI$_2$, ≥99.0%) and chromogenic reagent prepared by phosphoric acid (H$_3$PO$_4$, ≥85.0%), sulfanilamide (C$_6$H$_8$O$_2$N$_2$S, ≥99.5%), n-(1-naphthyl)-ethylenediamine dihydrochloride (C$_{12}$H$_{14}$N$_2$·2HCl, ≥ 98.0%) were used to the electroreduction of nitrate and the determination of nitrate, nitrite and ammonia concentrations using a spectrophotometer (DR 6000, USA). And a dc power supply (GD1795-5S, China) was used to the preparation of electrodes and removal of nitrate. Using an ice-water bath (DFY-5/20, China) and a thermostat water bath (ZNCL-GS 190*90, China) to control the experimental temperature. When no specified, all of the chemicals in this study were analytical reagent.

2.2. Preparation of NTEs

NTEs were prepared through an electrochemical anodization method, using a titanium substrate anode. Titanium substrates were polished using sandpaper (150 mesh) and washed with deionized water. And then dried naturally. The electrochemical anodization process was occurred in an electrochemical-two-electrode cell with 150 mL effective volume, with graphite as cathode, separated from the anode by 8 mm, with a DC power supply at 25 V for 5–120 min under room temperature. The electrolyte consists of acetic acid (volume of acetic acid:H$_2$O = 10:1) and hydrofluoric acid. NTEs were obtained in the electrochemical cell, as-prepared NTEs were rinsed in deionized water to remove the surface residues and dried naturally.

2.3. Preparation of ENTEs

ENTEs were carried out in an electrochemical-two-electrode cell with 100 mL effective volume, with as-prepared NTEs as anode and graphite as cathode, under room temperature using a DC power supply. The as-prepared NTEs were oxidized by low-level current value at 0.1– 0.2 A for 10 s–30 s in sulfuric acid electrolyte (volume fraction is 2%). After the oxidation of low-level current, the as-prepared ENTEs were rinsing in deionized water and drying naturally.

2.4. Batch experiments

The electrochemical reduction reaction were operated in a 100 mL cylindrical undivided electrolytic cell with a DC power supply. The Pt electrode and NTE or ENTE were assembled as the anode and cathode, respectively. The active area of electrodes both were 2000 mm^2, and the distance between anode and cathode was 8 mm. Initially, 100 mL of deionized water with nitrate (50 mg/L) and Na$_2$SO$_4$ (0.5 g/L) were fed into the electrolytic cell where Na$_2$SO$_4$ is to improve the conductivity of electrolyte. Then switched on the DC power at specified current density. The electrolysis after 60 min was ceased. And 1.0 mL sample was taken from the cell at 10, 20, 30, 60 min, respectively. A DC power supply with a current range of 0–5 A and a voltage range from 0 V to 100 V was employed to provide electric current. When no specified, all of the experiments in this study were operated at atmospheric pressure, 38 mA/cm^2 current density and room temperature. Other conditions were the same as above in Sections 2.2 and 2.3.

2.5. Analysis and characterization

The concentration of nitrate, nitrite and ammonia in electrolyte samples were analyzed using spectrophotometer by standard colorimetric method [30]. Nitrogen gas compounds concentration were quantified by mass balance. The morphology of as-prepared electrodes was characterized by FESEM (S-5500, Hitachi, Japan and Merlin, Germany). X-ray photoelectron spectra (XPS) was performed using an ESCALAB 250Xi (Thermo Fisher, USA) instrument with an Al Kα source to analyze the chemical composition and structure of compounds over as-prepared electrodes.