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Research paper

Fabrication of a Ti/TiO_2/NiO electrode for electrocatalytic nitrite removal

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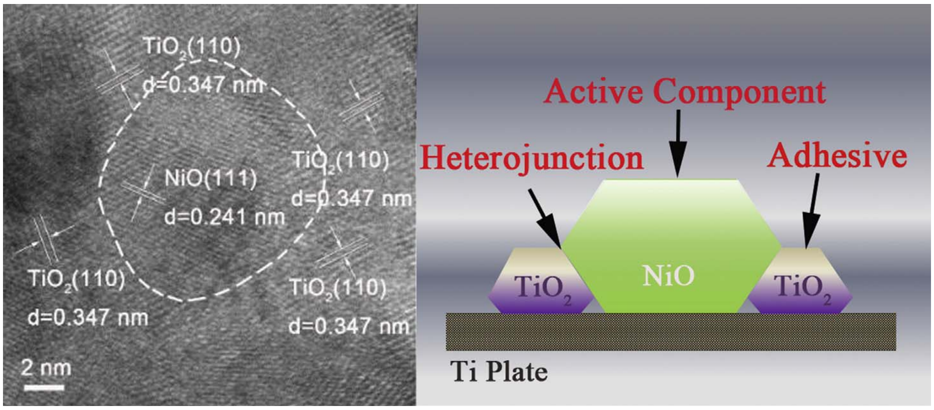
GRAPHICAL ABSTRACT



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ABSTRACT

Ti/TiO_2/NiO (Ti/TNO) electrode used for electrocatalytic oxidation of nitrite was fabricated by a simple thermal decomposition method in this work. The influences of calcination temperature on crystal phase and morphology of Ti/TNO composite were explored by XRD and TEM. After being calcined at 700 °C, NiO grains are closely surrounded by TiO_2 grains, in which TiO_2 acts as an adhesion agent to fix the NiO grains on the Ti plate. The relative contents of Ni(III) and Ti(III) species were found increase due to the close heterojunction between NiO and TiO_2, which reduces the impedance and improves the electrocatalytic activity of Ti/TNO. Ti/TNO-350-700 not only exhibits as high activity as those of Ti/TNO-350 and Ti/TNO-700 for electrocatalytic removal of nitrite contaminant, but also owns a superior electrocatalytic stability, which is more than 30 times and 2.5 times longer than those of Ti/TNO-350 and Ti/TNO-700, respectively.

1. Introduction

As an intensified chemical process, electrochemical oxidation, especially electrocatalytic oxidation, has been frequently concerned nowadays [1–3]. Due to the advantages of simple operations [4], high efficiency [5], low cost [6], and environmental compatibility [7], electrocatalytic oxidation has been extensively employed to deal with various inorganic and organic water pollutants [8–11].

Electrode materials play a crucial role on the effectiveness of the dynamic process [12]; a desired anode material is thought to have high electrocatalytic activity, good stability, low cost and no secondary pollution [13]. Traditional electrodes, such as carbon and graphite, are generally accompanied by surface corrosion that reduce their service life, while Pt anode undergoes poisoning phenomena [14,15].

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Dimensionally stable anode (DSA), therefore, has received much attention for superiorities of high electrocatalytic activity, mechanical and chemical stability and simple preparation methods [15].

As a typical DSA anode, Ti/RuO_2 is extensively used in chlor-alkali industry [16], and water electrolysis [17]. However, the relative rarity and high-cost of Ru element raise an imperative claim on developing alternative transition metal oxides to replace the RuO_2 for general electrocataytic applications. NiO is frequently investigated to substitute RuO_2 as water splitting electrocatalyst [18,19] and supercapacitor electrode material [20,21], owing to its excellent oxygen evolution activity, high theoretical specific capacitance, desired chemical stability, environmental friendliness and low cost [22–24]. Further, Ti/Ru-Ni-O anode was reported to own better chlorine evolution activity with low Ni content and promoted oxygen evolution with high Ni content [25]; the overall material's activity increases with increasing Ni content. Insertion of Ni into Co_3O_4 and the coexistence of NiO and $NiCo_2O_4$ can increase both the conductivity and active area for Co_3O_4, exerting a synergistic effect on oxygen evolution for Ti/Co—Ni—O anode [26].

Although NiO exhibits excellent performance in various composite catalysts, its electrocatalytic applications are greatly limited by its main drawback of low intrinsic conductivity. Therefore, enhancing the electrocatalytic activity of NiO-based electrode by improving its conductivity is meaningful for its actual applications. NiO-based materials such as CNT@NiO composite nanotubes [27], graphene/NiO nanosheets [28] have been reported as potential supercapacitor materials, in which the excellent electrochemical performances of materials are achieved due to the high electrical conductivity of CNT and/or the graphene matrix. The high resistivity of NiO itself as a drawback is however kept unresolved. Recently, the NiO/TiO_2 heterojunctions [29] and NiO—TiO_2 nanotube film [30] were found to facilitate charge transfer and therefore own better electrochemical performances. Although the intrinsic conductivity of both NiO and TiO_2 are poor, the interaction between them seems to effectively improve the electrochemical performance of the composite materials effectively. Therefore, Ti/TiO_2/NiO (Ti/TNO) electrodes were prepared in this work, in which the in-situ formed TiO_2 component from TiH_2 was utilized to mechanically stabilize NiO materials and promote the electrochemical performance of NiO materials. The electrical conductivity as well as electrocatalytic behavior of TNO electrode materials was explored, from which the heat treatment process was optimized for a better TiO_2—NiO interfacial interaction.

Recently, nitrite contamination has received particularly environmental concerns. Nitrite uptake causes serious hazards to the health of human and aquatic animals, for instance, inducing methemoglobinemia, liver damage, and cancer [31–33]. The hazard from aqueous nitrite contamination can be parried by oxidizing nitrite into nitrate with electrocatalytic oxidation method, in which the presence of chloride would promote the oxidation of nitrite by being transformed into active chlorine [34]. Due to its environmental significance, the nitrite elimination in surface water was selected as a model reaction to observe the electrocatalytic oxidation performance of Ti/TNO electrodes in this work.

2. Experimental section

2.1. Reagents and materials

$Ni(NO_3)_2 \cdot 6H_2O$, $NaNO_2$, H_3PO_4, NaOH and $C_2H_2O_4 \cdot 2H_2O$ were obtained from Shanghai Lingfeng Reagent. C_2H_5OH, sulfanilamide and *N*-(1-naphthyl) ethylenediamine dihydrochloride were obtained from Sinopharm Chemical Reagent. All the reagents were of AR and used as received. Ti plates (TA2 grade) were purchased from Shanghai Zhongmei Titanium Industry.

The water used in this work is a simulation of surface water of Qiantang River (Table S1) and was pre-prepared, in which the concentrations of chloride and sulfate were fixed at 30 mg L^{-1} and 40 mg L^{-1}, respectively, with a solution pH value of 7.8. Nitrite contaminant was then made by resolving desired amounts of $NaNO_2$ into the simulated surface water. The preparatory experiment results (Fig. S1) show that nitrite ion exhibits just similar electrocatalytic oxidation kinetics in the simulated surface water and Qiantang River water.

2.2. Preparation of Ti/TNO electrodes

Ti/TNO electrodes were prepared by a thermal decomposition method [35]. Ti plates with 0.5 mm × 4.5 cm × 7.0 cm in size were pretreated as the literature [3], prior to coating, among which, the acid etching by oxalic acid solution is utilized to make Ti plates rough. Typically, Ni^{2+} precursor solution (0.05 M $Ni(NO_3)_2$ ethanol solution) of 0.5 mL was brushed to one side of the pretreated Ti plate, which was then dried for 10 min at 100 °C. Similarly, the other side of Ti plate was also coated with another 0.5 mL Ni^{2+} precursor solution. The plate was then calcined at high temperature (350 °C, 400 °C, 500 °C, 600 °C or 700 °C) for 0.5 h to obtain the Ti/TNO electrode. The theoretical NiO loading is calculated as 0.059 mg cm^{-2} for Ti/TNO electrode after being coated once. According to the calcination temperature (T) used for Ti/TNO electrode preparation, the electrode is denominated as Ti/TNO-T. For instance, Ti/TNO-700 refers to the electrode that was prepared under 700 °C calcining.

Additionally, by repeating the coating and calcination (700 °C) process, Ti/TNO-700-x was prepared, of which x refers the coating and calcination times. For instance, Ti/TNO-700-4 refers the electrode that has been coated and calcined under 700 °C for 4 times. As a comparison, by coating Ni^{2+} precursor solution once more to the Ti/TNO-350-4 and then calcination under 700 °C, another Ti/TNO electrode was prepared, which is denominated as Ti/TNO-350-700.

2.3. Physicochemical characterization

Crystal structure of electrode material was measured with X-ray diffraction (XRD, Rigaku Ultima IV) operating in the reflection mode with Cu K*α* radiation. The chemical states of the elements in electrode material were measured X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi system with Al K*α* radiation) calibrated internally by carbon deposit C1s binding energy at 284.6 eV. The surface morphology of electrodes was analyzed with scanning electron microscopy (SEM, Tescan VEGA 3 SBU) and the micro-structure morphology of surface crystallites of electrodes was analyzed with high resolution transmission electron microscopy (HRTEM, JEOL JEM 2100F instrument operated at 200 kV).

2.4. Electrochemical measurement

The electrochemical properties of electrodes were monitored by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), which were performed on an electrochemical workstation (Zahner Co, Germany) with a Pt electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and Ti/TNO electrode as the working electrode with effective electrode area of 4.5 cm × 6.0 cm. The EIS spectra of electrodes were carried out in the 2.5 mM $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ (1:1) and 0.1 M KCl aqueous solution. The scanning scope ranged from 0.01 Hz to 10 MHz, the amplitude of the potential was 0.2 V and the bias voltage was 3.0 V. The measured EIS data were analyzed and fitted to the equivalent electrical circuits by ZSimp Win software. The CV tests were performed in the 10 mg L^{-1} $NaNO_2$ simulation surface water solution, covering the −3.0 V − 3.0 V potential interval at a scan rate of 100 mV s^{-1}.

2.5. Electrocatalytic oxidation test

The electrocatalytic oxidation of nitrite was carried out in a glass beaker containing 250 mL $NaNO_2$ simulation surface water solution