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A facile strategy to fabricate reduced TiO₂ nano-tube arrays photoelectrode and its high visible light photocatalytic performance for detoxification of trichlorophenol solution

Xiaoyong Deng^{a,1}, Ruonan Guo^{a,1}, Huixuan Zhang^a, Bo Li^{a,c}, Qjuling Ma^a, Yuqi Cui^a, Xinyi Zhang^a, Xiuwen Cheng^{a,c,*}, Mingzheng Xie^a, Qingfeng Cheng^{b,**}

^aKey Laboratory of Western China's Environmental Systems (Ministry of Education), Key Laboratory for Environmental Pollution Prediction and Control, Gansu Province, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, PR China

^bCollege of Resources and Environment, Chengdu University of Information Technology, Chengdu 610225, PR China

^cKey Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xinning Road 18, Chengxi District, Xining 810008, PR China

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ABSTRACT

In the research, reduced TiO₂ nano-tube arrays (denoted as R-TiO₂ NTAs) photoelectrode was successfully fabricated by potassium borohydride (PBH) reduction treatment. Afterwards, the as-fabricated photoelectrode was characterized by scanning electron microscope, X-ray diffraction, Raman spectra and electron spin resonance. Meanwhile, the optical and photoelectrochemical properties of R-TiO₂ NTAs photoelectrode were also studied through ultraviolet-visible diffuse reflectance spectroscopy and transient photocurrent response, respectively. The photocatalytic (PC) activity of R-TiO₂ NTAs photoelectrode was measured by degradation of trichlorophenol (TCP). Moreover, the change of toxic intermediates in the process of degradation TCP was further evaluated by photobacterium inhibition tests. Results suggested that an impurity level can be induced in the TiO₂ NTAs band gap by solution reduction treatment due to the generation of Ti³⁺ and oxygen vacancies (Ov). Furthermore, R-TiO₂ NTAs photoelectrode exhibited higher PC activities than that of pristine TiO₂ NTAs owing to the enhancement of visible light harvesting between 450 and 800 nm and separation efficiency of photogenerated electrons-holes (e/h⁺) pairs. The possible pathway for TCP degradation and photocatalytic mechanism were also proposed and confirmed. Furthermore, R-TiO₂ NTAs photoelectrode displayed good stability and reusability.

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1. Introduction

Chlorophenols (CPs), as a suite of recalcitrant and high priority contaminants, are extensively used in herbicides, insecticides, disinfectants and dyes and could be released into the environment while these products are being manufactured or employed [1–3]. They are also frequently made during industrial production and pollutant disposal. Moreover, trichlorophenol (TCP), as one of commonly CPs, can be found in natural water, soil and deposit sedi-

ment, as well as in living biosome. According to previous reports, TCP has a serious carcinogenicity to organism and could cause the formation of lymphoma/leukemia and liver tumors in mice [4]. However, conventional treatment technologies such as aerobic biodegradation and in-situ remediation hardly remove TCP from the environment because of its potent acute toxicity and persistence, and the release of which could have great impact on the environment and human health [5–8].

Recently, TiO₂ semiconductor, as one of the most acclaimed photocatalysts, has gained extensively interest within the scientific community because of its low cost, nontoxicity, high chemical stability and good photoelectric performance [9,10]. Acceptably, TiO₂ PC oxidation was available technology attributing to its prospective applications in pollutants elimination, air purification and photoconversion of CO₂ in recent years [11–13]. However, the vital defects were that TiO₂ nanomaterials possess wide band gap (~3.2 eV) and high recombination rate of photo-induced electrons (e⁻) and holes (h⁺) pairs [14,15]. The two major factors signifi-

* Corresponding author at: Key Laboratory of Western China's Environmental Systems (Ministry of Education), Key Laboratory for Environmental Pollution Prediction and Control, Gansu Province, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, PR China.

** Corresponding author at: College of Resources and Environment, Chengdu University of Information Technology, Chengdu 610225, PR China.

E-mail addresses: chengxw@lzu.edu.cn (X. Cheng), chqf185@163.com (Q. Cheng).

¹ Both authors contributed equally to this work.

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cantly restrict quantum yield of photocatalytic process and necessity to use of irradiation, so that its PC degradation activity of contaminants could be greatly lowered. In order to solve these problems, many different strategies were proposed, such as transition metal cations doping [16], nonmetals doping [17], dye sensitization [18], inorganic combination [19] and surface modification with precious metals and lower band gap semiconductors [20].

Ti³⁺ self-doped TiO₂ photocatalysts has been extensively studied because of enhanced visible light response and considerable photochemistry performance [21,22]. As demonstrated, the introduction of Ti³⁺ accompanied with the formation of oxygen vacancies by self-doping can induce a new energy level in the TiO₂ bandgap, which could narrow dramatically the band gap energy of TiO₂ [23,24]. Moreover, Ti³⁺ and oxygen vacancies have a spectral response in the region of visible light, thus having a significantly improved PC performance under visible light. Reduction treatment is efficient and economic strategy without introducing any impurity elements compared with the traditional doping ways, which is beneficial to remain the intrinsic crystalline structure [25]. Furthermore, our group had fabricated Ti³⁺ self-doped TiO₂ NTAs photoelectrode through a facile reduction process in the presence of PBH, which showed a commendable photoinduced charge carriers separation efficiency. However, it is still a significant challenge to find an appropriate and economic approach for fabrication of self-doped TiO₂ nano-catalyst.

The aims of this study were: (1) to synthesize R-TiO₂ NTAs photoelectrode using a facile solution phase reduction approach; (2) to investigate physicochemical properties of as-prepared samples; (3) to determine the photocatalytic activity of R-TiO₂ NTAs photoelectrodes by pollutants degradation under simulated sunlight irradiation and TOC removal and Cl release in the TCP degradation process; (4) to elucidate the possible degradation pathways of TCP by identifying the corresponding degradation intermediates; (5) to assess the change of intermediates toxicity during the photocatalytic degradation of TCP; (6) to clarify detailedly the enhanced PC mechanism of R-TiO₂ NTAs photoelectrode.

2. Experimental

2.1. Materials

Ammonium fluoride, glycerol, acetone, terephthalic acid, anhydrous sodium sulfate and potassium borohydride (KBH₄) were obtained from Sinopharm Chemical Reagent Co. Ltd and used without any further purification. In addition, trichlorophenol was purchased from Sigma-Aldrich. Ultrapure water was used throughout the experiments. Also, anhydrous ethanol and acetic acid was of HPLC grade.

2.2. Preparation of R-TiO₂ NTAs photoelectrode

According to previous reports by our groups, pristine TiO₂ NTAs photoelectrode was synthesized through anodization on the surface of Ti mesh using a typical procedure (cathode-anode device) [26,27]. Specifically, Ti meshes were firstly automatically polished with rough papers (200 meshes) before the anodization, then cleaned by ultrasound in C₃H₆O, C₂H₆O and ultrapure water for 10 min, separately, and then dried in the air. Afterwards, Ti meshes were brightened by diluted mixed acid (HF: HNO₃: H₂O = 1:4:5 in volumetric ratio) for thirty seconds to appear a glossy surface and were washed with ultrapure water repeatedly. Furthermore, TiO₂ NTAs were grounded on titanium foils via anodization in the electrolyte of 0.5 wt% NH₄F and 60% (v/v) C₃H₈O₃ in water. The reaction was carried out using a traditional two-electrode device with platinum as cathode and cleaned Ti mesh as anode. After that, the

as-prepared materials were rinsed with C₂H₆O and ultrapure water and dried at 378 K. Then, the obtained formless TiO₂ NTAs was fixed into the diluted potassium borohydride solution (0.5 mol·L⁻¹) for 20 min at room temperature followed by washing with water and ethanol and air drying. Eventually, the treated TiO₂ NTAs samples were calcined for 2 h at 873 K in a resistance furnace with 3 K min⁻¹ of heating-up rate.

2.3. Characterization

Wide-angle X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX III-3B diffractometer operating at 30 mA and 40 kV using monochromated Cu K α 1 radiation. SEM images were collected on a Quanta 200 F field emission scanning electron microscope (FE-SEM) at 20 kV. Samples for SEM imaging were fastened on specimen stub. A UV-2550 spectrophotometer equipped with an integrating sphere was used to obtain the reflectance spectra of the catalysts over the range of 200–800 nm, and BaSO₄ was employed as the reflectance standard. Raman spectrum was carried out by using a Jobin Yvon HR800 Raman spectrophotometer (equipped with Ar laser excitation wavelength of 457.9 nm). Furthermore, photoluminescence (PL) emission spectra for electron-hole separation and recombination rate were conducted by a Hitach FP-6500 at room temperature. BRIAN e-112 instrument was further used to identify electron paramagnetic resonance (EPR).

2.4. Photocatalytic (PC) activity of R-TiO₂ NTAs photoelectrode

In this study, TCP was used as target pollutants to evaluate the PC performances of R-TiO₂ NTAs photoelectrode. The photocatalytic (PC) experiments were performed in a cylindrical quartz photoreactor, which contained 80 mL of TCP (10 mg · L⁻¹). A 35 W Xenon lamp with illumination intensity of 67 mW·cm⁻² was employed as the light source to provide full-spectrum sunlight. Prior to illumination, R-TiO₂ NTAs photoelectrode was vertically fixed at the center of the photoreactor in the dark for 30 min. It was to ensure that the adsorption/desorption equilibrium of pollutants on the surface of the R-TiO₂ NTAs photoelectrode had been reached. Afterwards, Xenon lamp was switched on. At each irradiation time interval, the reaction solution was collected and then immediately filtrated and measured using a Shimadzu LC 10A high performance liquid chromatography equipped with a Kromasil KR100-5 C18 column (20 mm × 4.6 mm i.d.). Furthermore, we also detected the total organic carbon (TOC) values during TCP degradation using a TOC auto analyzer (Shimadzu TOC-VCPH, Japan). The release of chloride ions was monitored through an ion chromatograph (Dionex ICS3000). According to the Water Quality-Determination of the Acute Toxicity-Luminescent Bacteria Test (GB/T15441-1995), *Vibrio fischeri* (*V. fischeri*) was used to measure the change of toxicity.

2.5. Photoelectrochemical (PECH) measurements

The photoelectrochemical (PECH) measurements were investigated using a PQSTA128N electrochemical workstation in a 100 mL regular cylindrical quartz beaker through a three-electrode system with a platinum foil counter electrode and an SCE reference electrode, where the R-TiO₂ NTAs photoelectrode was used as the working electrode. The simulated solar irradiation source was supplied by a 35 W Xenon lamp. 0.1 mol·L⁻¹ Na₂SO₄ solution was used as supporting electrolyte.

3. Results and discussion

In order to investigate the change of microcosmic morphology of R-TiO₂ NTAs, The SEM images were displayed in Fig. 1. Seen from Fig. 1a, the alignment of nanotube structure queued closely

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