Applied Catalysis A: General 385 (2010) 114–122

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Combined potential of three catalysis types on TiO_2 nanotube (TNT)/Ti and nanoparticle (TNP)/Ti photoelectrodes: A comparative study

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ARTICLE INFO

Article history:
Received 31 May 2010
Received in revised form 29 June 2010
Accepted 30 June 2010
Available online 7 July 2010

Keywords:
Combined degradation
Photocatalysis
Electrocatalysis
TiO_2 nanotube (TNT)
TiO_2 nanoparticle (TNP)
Azo dye

ABSTRACT

The one-dimensional TiO_2 nanotubes (1D TNT/Ti) photoelectrode with a huge anodic area of 38 cm^2 were successfully prepared for the first time, with satisfactory morphological integrity, structural strength and distinguished photoactivity, and then utilized in a combined degradation system. A novel and photo-driven combined degradation system (TBPE system), which was functionally comprised of photon-efficient thin-film photocatalysis, conventional bulk-phase photocatalysis and photocarrier-efficient electrocatalysis, was developed on the vertically ordered and upright oriented 1D TNT/Ti rotating photoelectrode (TNT-TBPE system). Its properties were compared to those of the randomly packed zero-dimensional TiO_2 nanoparticles (0D TNP/Ti) rotating photoelectrode (TNP-TBPE system). Under the optimized operation conditions, the degradation of methyl orange (MO) was comparatively studied in the TNT-TBPE and TNP-TBPE systems. A 7.6–32.3% degradation enhancement and 20% larger stability indicated the excellent degradation activity and photochemical stability of TBPE system on novel 1D TNT/Ti compared to existing 0D TNP/Ti photoelectrode. The difference was attributed to the functional combination of these three catalysis types and the effective incorporation of 1D TNT/Ti rotating photoelectrode.

1. Introduction

TiO_2 photocatalysis (PC) has attracted considerable both scientific and engineering interest due to its distinguished performance for complete destruction of almost all kinds of organic pollutants, such as persistent toxic substances, dyes, pesticides and herbicides, under UV, visible or solar light irradiation. However, there are also several intrinsic drawbacks preventing its industrial application, i.e. mass transfer of oxygen, light penetration and electron–hole recombination, all of which would lead to a low photo-efficiency and deteriorative cost-effectiveness [1]. Recently, some photocatalysis types and photoreactor configurations were reported that could largely increase the photocatalytic efficiency and economic competitiveness, based on alleviating or even resolving some of the drawbacks [2,3].

Since photocatalytic oxidant species, mainly hydroxyl and peroxyl radicals, have very short lifetimes and are very easy to terminate; the PC occurs primarily on the surface and/or in very close proximity of the photocatalyst [4]. Consequently, the thin-film PC with only a thin water film between the light source and photocatalyst is suggested to get a larger illumination intensity per unit volume by reducing the invalid photon loss through absorption within the bulk-phase-filling liquid [5–14]. The similar thin-film biocatalysis type (Rotating Biological Contactors, RBCs) has been industrially applied in water and wastewater treatment plants (WWTPs) for several decades [15], the experience could provide informative guidance for the design and operation of photon-efficient thin-film PC. Compared to conventional bulk-phase PC, the novel thin-film PC is simple in design, operation and scaling [6,7,12,13], the major advantages include high illumination efficiency, good stirring, excellent photoactivity, no oxygenating and therefore attractive operation cost-effectiveness [16–18].

To further enhance separation, transfer and utilization efficiency of the highly active photocarriers as well as photoconversion efficiency and photocatalytic activity of the photo-driven degradation system for environmental purifications, the application of a low external bias potential to directionally drive photoelectrons and consequently prevent the rapid recombination/loss of powerful

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doi:10.1016/j.apcata.2010.06.053

photogenerated electron–hole pairs. The results were dramatically effective, the procedure is indeed the principle of photoelectrocatalysis (PEC) [19,20].

Up to now, the photon-efficient thin-film photochemical process has been studied mainly in PC [5–14] and seldom in PEC [14,20,21], with TiO_2 photocatalyst in the form of randomly packed zero-dimensional nanoparticle film (0D, TNP). However, some intrinsic bottlenecks, i.e. low surface area, poor light-collection efficiency, inefficient charge separation, transfer and utilization properties as well as the resultant low photo-driven activity, have been observed in this 0D TNP nanoarchitecture type, while more and more informative insights were gained into TiO_2 photocatalyst in the form of vertically ordered, upright oriented one-dimensional nanotube arrays (1D, TNT) [22–33].

Considering the significant superiority of 1D TNT/Ti over 0D TNP/Ti photoelectrode, in this study, we developed a novel and photo-driven combined degradation system (TBPE system) on the vertically ordered, upright oriented 1D TNT/Ti photoelectrode (TNT-TBPE) as a new photoelectrode type in the rotating disk photoreactor (RDPR). The depicted TBPE system was functionally comprised of three different catalysis types: photon-efficient thin-film photocatalysis, conventional bulk-phase photocatalysis and photocarrier-efficient electrocatalysis. Compared to previously reported functional combinations of catalysis types [5–14,20], one will find the superiority of the newly proposed TNT-TBPE system in two areas: (1) the incorporation of PEC instead of PC; (2) the incorporation of vertically ordered 1D TNT/Ti instead of randomly packed 0D TNP/Ti photoelectrode. Consequently, this combined system should be anticipated to possess remarkable superiority in quantum yield, utilization efficiency of photocarriers and the resultant oxidation potential. However, to the best of our knowledge, no studies have been reported regarding this novel TNT-TBPE system and its combined characteristics.

However, even though the vertically ordered, upright oriented anodic 1D TNT array possesses attractive advantages, i.e. stronger light-harvesting scattering and greater charge-collection efficiency, the preparation by regular chemical anodization technique on relatively large surface areas, such as 38 cm^2 in this study, would detrimentally involve the formation of NT bundle layers in the anodic films. Therefore, up to now, only a few reports are available for the "large-area" anodization [26,28,31,34–36], while the typical effective anodic area is no more than 1 cm^2, which could be named "small-area" anodization.

Therefore, the successful overcoming "bundling and curling" in anodic 1D TNT arrays is proved to play a predominant role in photoconversion efficiency [28,30]. The sensitized dye coverage was obviously greater in the more aligned NT arrays, which indicated that reducing intertube contacts could effectively increase the internal surface area of the photoactive films, and the incident photons conversion efficiency (IPCE) and responsive photocurrent density were highest in dye-sensitized solar cells (DSSCs) with more aligned NT arrays due to an significantly enhanced light-harvesting efficiency.

To our knowledge, in this study, we successfully prepared the vertically ordered, upright oriented 1D TNT/Ti photoelectrode on a large anodic surface area of 38 cm^2 for the first time, with satisfactory morphological integrity, structural strength and distinguished photoactivity. The materials were then utilized in the photon- and photocarrier-efficient combined TBPE system. The objective was to evaluate and validate the incorporation of vertically ordered 1D TNT/Ti disk as a new rotating photoelectrode type into TBPE system with the typical azo dye of methyl orange (MO). Comparisons to the randomly packed 0D TNP/Ti photoelectrode (TNP-TBPE) were available.

2. Experimental

2.1. Materials and reagents

Round titanium sheets (99.6% purity, diameter 70 mm; thickness 0.25 mm, surface area 38 cm^2) were employed for TNTs anodization. Ethylene glycol (EG) and Na_2SO_4 were employed as supporting electrolytes. The preparation of nanocrystalline films employed commercial TiO_2 (P25, Degussa AG, Germany, a mixture of ca. 30% rutile and 70% anatase, a mean size of about 25 nm, BET surface area 55 m^2/g). All chemicals were of reagent grade and were used as received, and aqueous solutions were prepared in doubly deionized water.

2.2. Photoelectrodes

TNT/Ti photoelectrode was prepared by anodic oxidation method. Before anodization, the circular Ti sheet was ultrasonically degreased successively in acetone and methanol for 30 min, respectively, then thoroughly rinsed with doubled-deionized water and evaporatively dried in air. For chemical anodization, a high-voltage power supply (WYJ-120V-2A, Shanghai Quanli Co., Ltd.) and a nickel foil (0.5 mm thickness, 150 mm × 150 mm size) as the counter electrode were employed. Then, the electrochemical preparation was performed in 98 vol.% EG + 2 vol.% H_2O + 0.3 wt.% NH_4F at room temperature in a typical two-electrode electrochemical cell; the anodization process consisted of a potential ramp (with a sweep rate of 5 V/min) from the open-circuit potential (OCP) to 40 V and a subsequent potential hold at 40 V for a duration of 6 h. After anodization, the high-temperature annealing treatment was employed at 450 °C for 3 h [34]. However, to avoid any possible damage to the mechanical stability of newly prepared TNT/Ti photoelectrode during postgrowth treatment, we avoided ultrasonic cleaning in this study, which was different from the cited literature.

TNP/Ti photoelectrode was prepared by spreading a viscous dispersion of colloidal TNPs on the same circular Ti metal support as was used for TNT/Ti photoelectrode [37]. The method for nanocrystalline films preparation employed the typical commercial TiO_2, P25.

For physical characterization, a field emission scanning electron microscope (FESEM; Hitachi, S-4700) was used to analyze the nanotube (NT) formation and morphology of the prepared photoelectrode samples. X-ray diffraction (XRD) analysis was done using a Philips-12045 B/3 diffractometer to identify the sample crystal structure, the target used in the diffractometer was copper (λ = 1.54 Å), and the scan rate was 1.2°/min.

Electrochemical and photoelectrochemical characterizations were performed in a three-electrode system with 0.01 M Na_2SO_4 aqueous solution in dark or under UV illumination, powered by a CHI 660d electrochemical workstation (Shanghai Chenhua Co. Ltd., China).

2.3. Combined degradation

The employed RDPR was reported previously [21], while the TNT/Ti and TNP/Ti photoelectrodes (surface area 38 cm^2) were comparatively employed in TNT-TBPE and TNP-TBPE systems, respectively. In the combined TBPE system, the upper half of rotating photoelectrode was exposed to open air and possessed the functional combination of photon-efficient thin-film photocatalysis and photocarrier-efficient electrocatalysis, while the lower half was immersed in the highly colorized sample solution and possessed the functional combination of conventional bulk-phase photocatalysis and photocarrier-efficient electrocatalysis.

During combined degradation in a TBPE system, the locations of photon-efficient thin-film photocatalysis and conventional bulk-