Applied Catalysis B: Environmental 193 (2016) 151–159

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Solar thermoelectric field plus photocatalysis for efficient organic synthesis exemplified by toluene to benzoic acid

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ARTICLE INFO

Article history:
Received 2 February 2016
Received in revised form 2 April 2016
Accepted 12 April 2016
Available online 14 April 2016

Keywords:
Photocatalysis
TiO_2 nanotubes
Solar
Thermoelectric
Benzoic acid synthesis

ABSTRACT

The solar thermal electrochemical process synthesis of benzoic acid is an efficient way for organic synthesis based upon solar energy utilization. Graphite and platinum anodes have been developed with high yield and selectivity of benzoic acid. In this article, we present the first demonstration of the solar thermal-electro-photo field for efficient benzoic acid synthesis by using TiO_2 nanotubes electrode. By adjusting the three-solar field process, toluene is oxidized at the surface of the photoactive, electrically driven, heat activated TiO_2 nanotubes electrode. Results showed that, the synergistic effect of the three fields was found for enhancement of toluene oxidation at TiO_2 electrode. The yield of benzoic acid and conversion of toluene is greatly improved with temperature, and arriving to 26.1% and 62.6% at 90 °C, respectively. In this process, solar thermal decreases the electrolysis potential of toluene oxidation. Hydroxyl, carboxyl and OOH groups, as well as the emergence of TiOC bond at the surface of the TiO_2 nanotubes electrode, lead to an increased UV and visible absorption and a significant enhancement of TiO_2 photocatalytic properties to increase the yield of benzoic acid. Simultaneously, an applied solar electric potential promotes the separation of photogenerated electrons and holes. As a result the efficiency of TiO_2 photocatalysis enhanced.

1. Introduction

The increase in consumption of fossil fuels, its eventual depletion and its associated environmental pollution have prompted a careful look at the issues dealing with our energy supply and demand [1]. The buildup of atmospheric carbon dioxide and its climate change consequences, and the ongoing, increasing demand for energy is forcing us to seek environmentally clean alternative energy resources [2]. Solar energy contributes an increasing role in energy production owing to its abundance, cost-competitiveness, and low associated carbon emissions, and great efforts have been devoted to develop new solar energy conversion systems. The direct conversion of solar energy to chemical energy for the production of renewable and nonpolluting materials remains a great and fascinating challenge for scientists [3,4]. A promising method of solar energy conversion for the synthesis of organic chemicals is artificial photosynthesis, but the efficiency of sunlight driven syntheses has remained low, and an alternative to light (alone) activated processes is needed.

The solar thermal electrochemical process, is an alternative solar energy conversion process. It achieves a high efficiency by matching solar-to-thermal and solar-to-electrical conversion for a specific molecular reaction or solar-to-chemical process. The process uses the full spectrum of sunlight, including the sub-bandgap (IR) spectrum that not accessible to solar cells, to lower the energy and facilitates the kinetics of useful endothermic chemical reactions [5–8]. Solar thermoelectric organic synthesis, as an efficient solar thermal electrochemical process, and has been used in benzoic acid synthesis from toluene [9,10], as simultaneously driven by a thermal collector and a photovoltaic.

In general, the direct oxidation of toluene is difficult to carry out, it needs harsh condition such as high temperature, high pressure or promotion by a catalyst [11]. Solar thermoelectric process provides an improved synthetic pathway by coupling solar electronic and solar thermal energies. Here we address the question of whether this process can be further improved by coupling solar UV, solar electronic and solar thermal energies at the same time, as solar

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http://dx.doi.org/10.1016/j.apcatb.2016.04.024
0926-3373/

is compatible with the high bandgap of TiO_2 which is known as photocatalyst.

Recently, solar energy conversion systems based on nanostructured elements have attracted considerable interest [12,13]. As the nanostructured materials such as nanocrystals or quantum dots, nanotubes, nanorods, and nanowires, can significantly improve charge collection efficiency [14,15]. Among various sunlight responsive materials, titanium dioxide (TiO_2) is a widely studied inexpensive, commercially available, non-toxic and chemically stable photocatalyst [16–18]. Apart from water treatment applications [19,20], TiO_2 has been extensively employed in air purification [21,22]. TiO_2 has three metastable phases: rutile, anatase and brookite. The anatase crystalline phase is desired due to its stronger response under UV irradiation [23]. The wide bandgap energy of TiO_2 means higher energy from UV light is required to excite electrons to produce hydroxyl radicals, which is the key to the photoreaction of chemicals in the presence of oxygen [24,25]. Arrays of TiO_2 nanotubes with anatase crystalline have been widely used to facilitate optical absorption and collection of UV [26].

Herein, we report a more comprehensive solar thermoelectric process for solar energy utilization, a reaction driven simultaneously by three-solar field, in which solar-thermal, solar-electricity and solar-photo has been used in one system for benzoic acid synthesis from toluene. In this 3-field mode, TiO_2 nanotubes are utilized as the electric and light driven anode. The photoactive electrode is prepared by calcinating the anodized TiO_2 nanotubes at the temperature of 450 °C to obtain a large surface area and strong activity of photocatalysis. The reactant (toluene) was oxidized (to benzoic acid) at the TiO_2 nanotubes film electrode. The conversion of benzoic acid increased with the combined application of solar-thermal (higher temperature), an applied stable solar photovoltage, and solar photons. The TiO_2 nanotube electrode is characterized by SEM, EDS, FTIR and XRD. The composition of products from toluene oxidation (benzyl alcohol, benzaldehyde, and benzoic acid) is determined by gas chromatography (GC). The mechanism of the photocatalysis of toluene at TiO_2 nanotube electrode is explored, and the synergistic effect of solar thermal, solar electricity and UV part of sunlight on the reaction process of benzoic acid formation was demonstrated for the first time.

The synthesis rate of benzoic acid is 0–8.9% with the application of a single solar field (either photo-activated, the separate application of solar thermal or solar electronic energy) and increases to 26.1% in the three-field of solar energy process. In this three-field experiment, the overall conversion of toluene reaches 62.6% at 90 °C with the aid of 1.0 V stable voltage of photovoltaic and UV sunlight. All energy for this benzoic acid synthesis at TiO_2 nanotubes electrode comes from solar thermal, solar electricity and solar photo, these three fields of solar energy process are well matched to function simultaneously with each other.

2. Experimental section

2.1. Chemicals and materials

A 2 mm thick titanium sheet (99.6%, Stream Chemicals) was cut into pieces of $20 \times 10\,mm^2$. Ethylene glycol ($(CH_2OH)_2$, EG), ammonia fluoride (NH_4F), acetone (CH_3COCH_3) were purchased from Xinlian Organics and used as received. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MU cm that was prepared by a Millipore system. Benzoic acid (C_6H_5COOH, ZT Co., LTD, 99.5%), toluene ($C_6H_5CH_3$, YX Chemical Co., LTD, 99.5%), Benzaldehyde (C_6H_5CHO, CL Co., LTD, 98.5%), Sodium dodecyl benzene sulfonate ($C_{18}H_{29}NaO_3S$, XW Co., LTD), Sodium hydroxide (NaOH, PK Chemical Co., LTD, 99.5%) and Sulfuric acid (H_2SO_4, LT Chemical Co., LTD, 98%) were used in the solutions.

2.2. Preparation of TiO_2 NTs

The TiO_2 nanotubes electrode on the Ti substrate was fabricated in the following manner. The TiO_2 NTs film was obtained using the anodization process in an electrolyte solution containing 0.2 g NH_4F, 1.2 mL deionized water and 60.0 mL glycol. Prior to anodization, the Ti sheet was first degreased by sonicating in acetone, ethanol and room-temperature deionized water for 15 min respectively. The anodization was carried out by using a conventional two-electrode system with the Ti sheet as an anode and a Pt gauze (Aida, 52 mesh) as a cathode, the Ti sheet was anodized at 50.0 V for 30 min. After the anodization, the prepared TiO_2 NT samples were cleaned with DI water and dried in air. Finally, the sample was annealed at 450 °C for 2.0 h with heating and cooling rates of 10 °C min^{-1}, the anatase TiO_2-film can be fabricated.

2.3. Solar thermal-electricity-photo process for benzoic acid synthesis

The synthesis of benzoic acid was experimentally characterized in a synergy of combined solar thermal, solar electricity, and solar photo energies. The as-prepared TiO_2 electrode ($1.0 \times 1.0\,cm^2$) and Pt-counter electrode ($1.0 \times 1.0\,cm^2$) were assembled into a sandwich-type electrolyzer. A Keithley 2601 source meter was used to collect data, and collimated light ($\lambda > 300$ nm, 100 mW/cm^2) from an Oriel 300 W xenon arc lamp was used as the light source to simulate AM 1.5 illumination (100 mW/cm^2). The photooxidation activity of TiO_2 nanotube electrode was evaluated by matching the photoreaction of toluene experimental setup with the coupling mode of solar thermal and solar electricity process for benzoic acid synthesis as previously detailed [9], and in this study also with, and without, illumination under UV light. Before experimentation, the 100 mL solution of the 0.05 M sulfuric acid and 0.001 M surfactant is placed into the electrolysis cell and was stirred for 1.0 h in the dark to reach the adsorption-desorption equilibrium, and then the toluene is added to the reaction chamber with 200 ppm at the voltage of 1.0 V from solar electricity. The initial photocurrent at an applied 1.0 V photopotential increases from 0.01 mA cm^{-2} at 30 °C to 0.15 mA cm^{-2} at 90 °C. Repeat the above experiment by illuminating the devices, and control the temperature (30 °C, 60 °C or 90 °C) for 0.5–1.0 h until the current decreases tenfold, at which point the electrolysis can be terminated, and the outdoor experimental apparatus are shown in Fig. S1. The separation of the crude product has been detailed in our previous article [9]. The product can be characterized by Gas Chromatography, and the analysis of SEM, FTIR, XRD, EDS of TiO_2 electrode has been carried out.

The single field experiments, including solar thermal, solar electrical, and solar photo (directly usage of sunlight) field driven process for benzoic acid synthesis, are also carried out on the solar thermal-electricity-photo process. The configuration of the electrolyte, reactant and other operations are the same thing of the 3-field. Similar situation applies to the coupling effect of solar energy (ST, SE, SP) for benzoic acid synthesis, that is the efficiency of pair-wise combinations (simultaneous application of two of the three individual) of solar energy field.

2.4. Characterization of TiO_2 NTs

IR-spectra were measured in KBr pellets from 4000 to 400 cm^{-1} using a Tensor 27 FTIR spectrometer to detect the changes produced by groups at the surface of the TiO_2 electrode before and after benzoic acid synthesis with synergistic of solar thermal, solar electricity and solar photo. The morphologies of the TiO_2 electrode were obtained by scanning electron microscopy (SEM, Quanta 200) and the compositions on the film were measured by Energy Dispersive Spectrometer (EDS). The crystalline structure was analyzed by