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Electrochemically assisted photocatalytic degradation of methyl orange using anodized titanium dioxide nanotubes

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ABSTRACT

The TiO_2 nanotubes have demonstrated potential in the photoelectrocatalytic degradation of methyl orange dye (MO). TiO_2 nanotubes were prepared using anodization of titanium foils in phosphoric acid (PA) and ethylene glycol (EG) by mechanical stirring and ultrasonic method. The TiO_2 nanotubes prepared in EG under ultrasound followed by annealing in nitrogen atmosphere showed higher activity towards dye degradation as compared to the stirring method. Dye degradation shows improved activity under an external bias compared to degradation performed in the absence of an external bias. An increase in the external bias from +0.0 to +0.1 V versus calomel electrode (SCE) is sufficient to improve the degradation rates of MO from 22% to 57% within the first 10 min. At +0.1 V, a complete degradation of 40 μM MO is observed within 30 min. The addition of oxidants such as oxygen and hydrogen peroxide demonstrate improvement in the MO degradation.

1. Introduction

The presence of dye pollutants in the wastewater streams from the textile industry are of an enormous environmental concern. It is estimated that nearly 15% of the dye is lost during dyeing processes and is released into wastewater streams [1]. These dyeing effluents can have toxic effects on the ecosystem, especially on microorganisms, and its long degradation time in the environment is a cause for concern. A variety of physical, chemical, and biological methods are presently utilized in wastewater treatment systems. Though biological treatment is a proven technology and is cost-effective, it has been reported that the majority of dyes are only adsorbed on the sludge and are not degraded [2]. Physical methods, such as ion-exchange [3], adsorption [4], air stripping [5], etc., simply transfer the pollutants to another phase rather than destroying them.

Titanium dioxide has emerged as the leading candidate to provide complete destruction of organic pollutants via heterogeneous photocatalysis that result in total mineralization of many organic pollutants [6,7]. Several studies have been reported of using TiO_2 slurry in photocatalytic degradation of different dyes [8–10]. Though this process offers actual annihilation of the dye molecules at a very high efficiency, the post-treatment recovery of TiO_2 can be costly [11]. Thus several researchers have investigated the possibility of immobilizing TiO_2 on a substrate as a film to counter this problem [12,13]. For example, Boldrin and coworkers have demonstrated the use of sol–gel TiO_2 film on a titanium metal support [14–17]. However, there is a risk of a significant reduction of active surface area when the TiO_2 particles are cast as films. This causes the degradation time to be prolonged [18].

Recently, the synthesis of TiO_2 in the form of hollow nanotubes (NTs) over a titanium substrate has been demonstrated [19]. These nanotubes are typically produced by anodic oxidation of the titanium foil in various electrolytes [20,21]. They have demonstrated interesting photoelectrochemical activity that mainly includes water splitting [22]. A few articles on the photocatalytic degradation of pollutants have also been reported [23–25]. Different methods of producing nanotubular array of titanium dioxide that yields high photocurrent has been reported [21,22].

There are several reasons for evaluating the photocatalytic properties of TiO_2 nanotubes for dye degradation. Compared to TiO_2 nanoparticles, there are fewer interfacial grain boundaries in TiO_2 nanotubes. This has been reported to improve the redox catalytic properties at the TiO_2 surface [26]. The presence of less grain boundaries also assists in promoting charge (electron-hole) transport. Improved charge transport is known to favor photocatalytic degradation of pollutants [23]. Finally, the dimensions of the nanotubes are such that space charge layer (and related electronic properties such as band gap) in the nanotubes promote electron-hole pair separation [27]. This can also improve photocatalytic dye degradation.

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In this paper, we have examined the photocatalytic degradation of a model dye, methyl orange (MO), over TiO_2 nanotubular anode. Methyl orange, which belongs to the azo dyes family, and is known to be carcinogenic and mutagenic, has been studied by Boldrin and coworkers [14]. We have prepared the TiO_2 nanotubes in different electrolytes by adapting an earlier reported procedure [28]. The work reported in Ref. [28] has been focused on the preparation methods of the TiO_2 nanotubes and the formation mechanism during anodization. The work reported herein compares different methods for TiO_2 nanotube synthesis and identifies the most promising method specifically from an application (i.e. photocatalytic degradation) point of view. Further, the application of external bias, effects of different oxidants on the photocatalytic degradation of dye, and an insight into the effects of additives on degradation mechanism is also presented here.

2. Experimental

2.1. Chemicals

Phosphoric acid (H_3PO_4, Fisher, 85% in water), sodium fluoride (NaF, Fischer, 99.5%), ammonium fluoride (NH_4F, Fischer, 100%), ethylene glycol ($C_2H_4(OH)_2$, Fischer), deionized water (Millipore Q®), acetone (Aldrich, 99.5%, diluted to 50%), methyl orange (Sigma), and hydrogen peroxide (H_2O_2, Aldrich, 35 wt.% in water) were used as received without further treatment. The titanium foil thickness was 0.2 mm (ESPI Metals, 99.9% purity).

2.2. Preparation of TiO_2 nanotube array

Rectangular strips (1 cm × 4 cm) of titanium foils were cut out, and were washed in acetone under ultrasonication for 5 min. Nanotubular TiO_2 arrays were formed by anodization of the titanium foils in 400 mL of electrolytic solution using 20 V_{DC} bias (Agilent E3649A DC Power Source) for 60 min. A two-electrode configuration was used for anodization against a flag shaped platinum cathode (thickness: 1 mm, area: 3.75 cm^2). The distance between the two electrodes was kept at 4.5 cm in all experiments. Only 3.5 cm of the Ti foil length was submerged in the anodization medium.

Two different anodization media – aqueous and non-aqueous – were used in these experiments to compare its effect on photodegradation reaction. The aqueous medium consisted of phosphoric acid (PA) solution (0.5 M H_3PO_4 and 0.14 M NaF). The non-aqueous medium was ethylene glycol (EG) solution (0.5 wt.% NH_4F and 10 wt.% distilled water). For both types, two different agitation mechanisms were utilized—magnetic stirring (S) and ultrasonication (U). The stirring speed was maintained at 100 rpm (Corning Stirring Hot Plate PC-420D), and the ultrasonication was carried out at 42 kHz (Branson 3510 Ultrasonicator). The four different types of samples will be referred to as PAS, PAU, EGS, and EGU here forth.

2.3. Annealing of samples

All samples were heat treated by annealing under nitrogen atmosphere at 500 °C in a tube furnace (Thermo Scientific, Lindberg Blue M BF51866C). The furnace was ramped up at a rate of 1 °C/min, and was maintained at 500 °C for 2 h. It has been reported that TiO_2 NTs prepared using EG as the anodization medium exhibits higher photoactivity for water electrolysis reaction when annealed in hydrogen atmosphere [28]. To examine the effect of annealing condition on the photocatalytic degradation process, EGU samples have been prepared in both nitrogen and hydrogen atmosphere (EGUN and EGUH, respectively, here forth).

2.4. Characterization

The scanning electron micrograph of EGUN samples was obtained using Hitachi S-4700 FE-SEM. An energy dispersion spectroscopy (EDS) analysis identifying the composition of nanotubes is also reported. The glancing-angle X-ray diffraction pattern was obtained using Philips-12045 B/3 diffractometer. The Cu Kα irradiation source was utilized at 40 kV.

2.5. Photocatalytic degradation of methyl orange

A 40 μM solution of MO was prepared in distilled water. This concentration was chosen for its UV–vis spectrum exhibiting absorbance near but below 1.0. A custom-made three-arm cell (one arm each for a working, counter and reference electrodes) was used for all photocatalytic degradation experiments. The cell holds approximately 7 mL of solution at a level where the TiO_2 electrode was submerged just below the anodization line (∼3 cm). A UV–vis light source was used to illuminate the TiO_2 photoanode (Newport 66902, Oriel Research). The far-UV radiation was filtered out using 0.5 M copper sulfate solution. The anode was kept at a 5 cm distance from the light source. The luminescence intensity was measured to be ∼90 mW/cm^2 at the photocell surface.

A potentiostat (Autolab PGSTAT 302) was used to apply an external bias during the degradation experiments. The effect of decreasing applied bias voltage was tested at +0.6, 0.5, 0.4, 0.3, 0.2, 0.1, and 0 V and under no bias conditions with respect to saturated calomel electrode (SCE). All voltages reported are versus SCE unless otherwise noted. A UV–vis absorption spectrum was obtained at 0, 10, 20, 30, 40, 50, and 60 min during the degradation experiments (Shimadzu UV2501 PC). Approximately 1 mL of the MO dye solution was taken out to obtain the spectrum and returned to the cell once the measurement was finished. The percent degradation was measured by the change in peak absorbance (at 464 nm) with respect to the absorbance at 0 min.

2.6. Effect of presence of oxidants

To investigate the effect of presence of oxidizing species, 0.5 mL of hydrogen peroxide (7.1 vol.%, 2.64 wt.%) was added to 6.5 mL of 40 μM MO solution. The experiments were performed with an external bias of +0.0 V versus SCE and also at no bias conditions under illumination. All other conditions were kept constant. The effect of oxygen saturation on photodegradation rate was studied by saturating 7 mL of 40 μM MO dye solution for 10 min prior to UV–vis illumination.

3. Results

3.1. Comparison of various anodization and annealing conditions on MO degradation

Fig. 1 shows the changes in the absorption spectra of an aqueous MO solution during the photodegradation process over the TiO_2 nanotubes. The spectra were taken at 10 min intervals of time following UV–vis illumination. The data in the figure shows the photocatalytic degradation of MO over PAS TiO_2 sample at +0.6 V in ambient condition. The absorbance spectra shown in the figure are representative of the trend noticed with other TiO_2 samples as well. The spectrum at $t = 0$ is the absorbance exhibited by the dye after equilibration in the dark with TiO_2 prior to photo-illumination. At $t = 60$ min of photo-illumination, a 54% decrease in the peak absorbance is observed. The decrease in the absorbance of MO with time was different in the presence of PAU, PAS, and EGS samples.