

Adsorption and photodegradation of methylene blue using a bulk Ti material with porous titania layer prepared by chemical oxidation



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ABSTRACT

In this study, a chemical oxidation method was adopted to prepare a porous titania network on Ti bulk for dye adsorption and photodegradation. The prepared titania layer was characterized by SEM, AFM, ATR-FTIR, XRD, and zeta potential. Using a longer oxidation time (90 min), a thicker titania layer ($\approx 4 \mu\text{m}$) with pH_{PZC} (pH of the point of zero charge) of ca. 2.2 and larger fraction of anatase phase could be formed. The prepared titania layer exhibited a better adsorption capability for MB (methylene blue) at various pH values than the commercial P25 TiO_2 nanoparticles ($\text{pH}_{\text{PZC}} = 6.0\text{--}6.8$). Moreover, the effect of surface roughness on dye photodegradation was investigated. With UV irradiation, it took 6 h to completely decompose MB using the titania layer prepared from the polished surface, whereas only half time was required by that abraded via #240 sandpaper. An improved dye photodegradation efficiency was achieved by a rougher surface for providing a larger surface area.

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1. Introduction

Titania is well-known as a cheap, stable, and effective catalyst successfully applied to adsorption and photodegradation of contaminants from industrial and domestic wastewaters, e.g. dyes, phenolic compounds, cyanotoxins, and other organic chemicals [1–20]. The adsorption capacity and photocatalytic activity of titania are significantly affected by several factors such as crystal phase [15,17,21–25], particle size [15,17,21,23,24,26–28], surface hydroxyl content [28,29], and morphology [30]. Accordingly, titania preparation method plays an important role in its subsequent performance of adsorption and photocatalysis.

The great majority of titania researches about pollutant adsorption and photodegradation focused on the powder form which can offer large surface areas. However, the uniformity of fine particle suspension in liquid as well as the following solid–liquid separation are the most challenging problems for industrialization and recovery [5,7,10,31–34]. Alternatively, bulk supporting material with immobilized titania is a choice for eliminating the drawbacks of fine powders [31–34]. Even though bulk material

may exhibit lower surface area, it is still an important field of titania research.

In our present study, a porous titania network could be formed on a bulk Ti material via a simple chemical oxidation in H_2O_2 solution. This titania layer was subsequently applied in the adsorption and photodegradation of dye from water. Dyes are extensively utilized in the industries of textile, paint, paper, leather, ink, etc. [4,11,35,36]. As an inevitable consequence, a great quantity of dye pollutants is lost during the manufacturing process. Effective treatments on dye wastewaters become very crucial for protecting our living environment [15]. Titania photocatalyst is a popular material for this purpose. By using the porous titania layer prepared in this work, the batch adsorption performances for cationic dye MB (methylene blue) and anionic dye CB (cibacron blue 3GA) at various pH values were investigated. Furthermore, the influences of titania preparation conditions (e.g. surface polishing degree and chemical oxidation time) on MB adsorption and photodegradation efficiencies were evaluated.

2. Materials and methods

2.1. Materials

Ti bulk materials (purity = 99.7%, disk diameter = 15 mm, thickness = 1 mm, density = 4.57 g/cm^3) were bought from Ultimate Materials Technology, Taiwan. P25 TiO_2 (purity > 99.5%,

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average particle size = 20 nm, density = 0.1 g/cm³, specific surface area = 50 ± 15 m²/g, anatase:rutile ≈ 4:1 [4]) is a commercial powder product from Degussa Company. H₂O₂ solution (30 wt.%) and CB (cibacron blue 3GA, C₂₉H₂₀ClN₇O₁₁S₃, MW = 774.16, 55% in purity) were purchased from Sigma–Aldrich. MB (methylene blue trihydrate, C₁₆H₁₈ClN₃S·3H₂O, MW = 373.9, 99.9% in purity) was supplied by ICN Biochemicals. The two dyes were used as supplied without further purification, and the fraction of inert material was not taken into account in the calculation of dye concentrations. Their molecular structures are depicted in Fig. 1. Moreover, sodium hydroxide and nitric acid from Showa were adopted to adjust the pH value of dye solutions.

2.2. Preparation of titania layer on Ti bulk by chemical oxidation

Three levels of surface roughness were investigated in this study. First, the Ti bulk was abraded by #240 SiC abrasive sandpaper to create the roughest case denoted as the #240-abraded surface. Additional surface treatment using #1200 sandpaper was then applied on the #240-abraded surface to obtain the #1200-abraded surface with medium roughness. Finally, the finest case designated as the polished surface was attained by further abrading the #1200-abraded surface with #2500 sandpaper followed with the polishing of 1 and 0.3 μm Al₂O₃ powders in sequential.

After a certain surface treatment, the Ti bulk was washed by acetone, ethanol, and deionized water (18.2 Ω), sequentially, in an ultrasonic cleaner. To carry on a chemical oxidation, the Ti bulk was immersed in 20 mL of 30 wt.% H₂O₂ solution at 95 °C for a certain time. Next, the Ti bulk was rinsed by deionized water in an ultrasonic cleaner for 1 min, and finally dried in an oven at 60 °C for 12 h.

FE-SEM with EDX (JSM-6700F, JEOL) was used to examine the 2D morphology of the Ti bulk surface and analyze the elements of the prepared titania layer, while AFM (SPA-400, Seiko) was

employed for the 3D morphology. The force constant of AFM probe was 40 N/m, and the scanning settings were: tapping mode, 1.0 Hz, and 100 μm². The roughness parameter Ra was determined by surface roughness tester (Surfcom 480A, Carl Zeiss, Ln = 0.25 mm, Vs = 0.05 mm/s). ATR-FTIR (FT/IR-4100, JASCO) was adopted to analyze the functional groups on the Ti bulk surface. The scanning was performed in the range of 4000–400 cm⁻¹ at a resolution of 1 cm⁻¹. To characterize the crystallographic structure of the Ti bulk surface by XRD (D8 Discover SSS, BRUKER), the sample was scanned at a 1.2°/min scanning rate using Cu Kα radiation with λ = 0.15416 nm, 40 kV, and 25 mA. In addition, the pH_{pzc} (pH of the point of zero charge) for the powders scraped from the prepared titania layer (2 mg in 10 mL of water) was determined with a zeta potential meter (Zetasizer Nano-ZS, Malvern). The powder properties were measured with BET (ASAP 2010, Micromeritics) and particle size analyzer (90 Plus, Brookhaven Instruments).

2.3. Batch adsorption and photodegradation of dyes

10 mL of aqueous dye solution at a certain pH value was placed in a vial with one piece of Ti bulk disk or 5.5 mg of TiO₂ powders. Batch adsorption experiment was conducted in the dark at room temperature for 3 h. Dye concentration was measured by a UV/vis spectrophotometer (UV-1601, Shimadzu). The detection wavelengths of MB and CB were 655 and 600 nm, respectively. The calibration lines obtained were Abs_{MB} = 0.6482 × C (10⁻⁵ M) and Abs_{CB} = 0.1350 × C (10⁻⁵ M). The dye adsorption capacity was determined from the difference between the concentration initially added and that remained after adsorption.

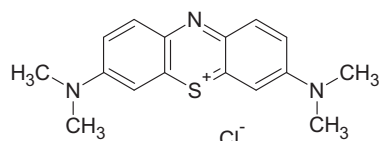
The photodegradation experiment was carried out at room temperature under UV irradiation at 365 nm, 8 W × 4 (F8T5BLB, Sankyo Denki). The distance between UV-light and Ti bulk was about 7 cm, and only the surface facing to the light was illuminated.

3. Results and discussion

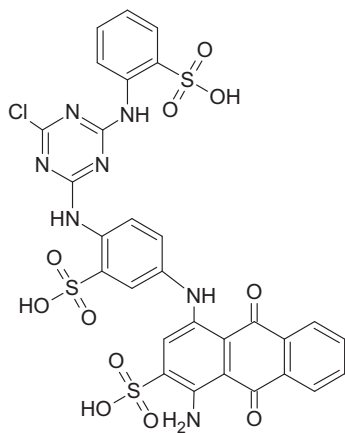
3.1. Characterization of the prepared titania layer

Fig. 2 presents the AFM and SEM photos for the Ti bulk surfaces after different surface treatments. Wide grooves were created on the surface abraded by #240 sandpaper, whereas narrower ones were observed for the #1200-abraded surface. After H₂O₂ oxidation, porous titania networks were formed on all the Ti bulk surfaces. However, cracks appeared on the surfaces treated by #240 and #1200 sandpapers. For the comparison of surface roughness, the related Ra values are listed in Table 1. Roughness was strongly affected by the degree of surface polishing, and a higher degree of polishing resulted in a smaller Ra value. In Fig. 2, the polished surface exhibited a more uniform pore structure, while the #240 abraded surface had the bumpiest appearance.

The ATR-FTIR spectra of the Ti bulks (polished surfaces) before and after H₂O₂ oxidation for 90 min are displayed in Fig. 3. As expected, no peaks were shown for the original Ti bulk. After H₂O₂ oxidation, the titania layer was formed on the surface and its characteristic bands were observed at 1428, 1620, and 3300 cm⁻¹.



methylene blue (MB)



cibacron blue 3GA (CB)

Fig. 1. Molecular structures of methylene blue (MB) and cibacron blue 3GA (CB).

Table 1

Surface roughness and MB adsorption capacities ($C_0 = 2.1 \times 10^{-5}$ M, pH 6.5, room temperature, 3 h) for the titania layers formed from Ti bulks with different surface treatments (oxidation time = 90 min).

Degree of polishing	Ra (μm)	MB adsorption capacity (μg/disk)
Polished	0.13 ± 0.01	39.0 ± 3.0
#1200 abraded	0.33 ± 0.01	50.1 ± 4.7
#240 abraded	0.51 ± 0.05	60.1 ± 1.0

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