

Fluoride-free Anodization of Titanium and the Photocatalytic Behaviour of the Produced TiO₂ Nanostructures

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Abstract

Current methods for anodizing titania to produce immobilized titanium dioxide (TiO₂) photocatalyst require the use of hazardous fluoride electrolytes. A fluoride-free electrolyte anodization method was developed. The electrolytes tested in this study were both bromide- and chloride-based and contained ethylene glycol as an additive. Under optimized anodization times and temperature conditions the alternative electrolytes led to growth of stable immobilized TiO₂ layers. Crystal phases and topography of the produced TiO₂ layers were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoelectron spectroscopy (XPS). Photocatalytic experiments showed that differences in the crystal phases had a strong effect on the degradation of the model aquatic contaminants carbamazepine and phenol. Nitrogen doping using urea made the photocatalyst more efficient by red shifting light absorption from UV into the visible region. The photocatalytic ability of fluoride-free anodized immobilized TiO₂ photocatalysts has previously not been investigated. Using electrolytes without fluorine can be a more sustainable and a safer way to produce immobilized TiO₂.

Keywords: photocatalysis, titanium dioxide, Phenol, hydroxyl radical, electrochemical anodization

1. Introduction

Organic trace contaminants, also termed micro-pollutants, such as pharmaceuticals, drugs, hormones and pesticides are insufficiently removed by conventional wastewater treatment methods. Micro-pollutants occur in treated wastewater at nanomolar to micromolar concentrations and may pose great risks to aquatic ecosystems (Kanakaraju, Glass et al. 2013). Some micro-pollutants have even been found in

drinking water. One way of removing micro-pollutants from water is to apply advanced oxidation processes (AOP) that utilise the oxidative power of hydroxyl radicals to destroy the contaminants. The hydroxyl radical can be produced via various routes, for example through photocatalysts. Titanium dioxide (TiO₂) is the most commonly used heterogeneous photocatalysts, which displays high efficiency, photo stability, as well as chemical and biological inertness (Chan, Wu et al. 2011, Ibhaddon and Fitzpatrick 2013). Immobilized photocatalysts are an attractive option, which does not require post. The production of immobilized TiO₂ photocatalysts is challenging, usually requiring a complex procedure. Anodization is an electrochemical method, used to produce tailored oxide layers on metal surfaces. By applying a defined current to the metal anode in an electrolyte solution, leads to the dissolution of the metal surface and the oxide layer formation. Hazardous fluoride based electrolytes, such as hydrofluoric acid (HF), are the most commonly used electrolytes to produce TiO₂ (Regonini, Bowen et al. 2013). Other more sustainable halide based electrolytes such as NaCl, as well organic solvents like ethylene glycol, have been shown to be effective at and aiding the production of an oxide layer. As well as electrolyte composition, other anodization parameters such as temperature, pH, voltage and time are key, to tailor which nanostructures form. The goal of this study was to develop a TiO₂ wire anodization method without the use of harsh chemicals and then characterize the photocatalytic ability of the anodized wires. Degradation of phenol and carbamazepine in a tubular photo-reactor designed to optimize the illumination of the photocatalysis surface thus enhancing degradation was also used.

2. Materials and Method

An anodization rig was designed and assembled to anodize a titanium wire to produce a TiO₂ layer on the surface. Anodizing conditions included an electrolyte solution of 0.3 M NaCl, 0.3M KBr in aqueous solution or with ethylene glycol, with an applied current of 0.2A. The addition of urea was used to dope the TiO₂ sample with nitrogen. The TiO₂ surface was investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The photoreactor used, has a tubular annular design, with a quartz tube containing the TiO₂ wire sitting between three UV lamps (shown in figure 1). The reaction solution is maintained at 10°C in a jacketed beaker and circulated through the reactor. The degradation of phenol and carbamazepine was monitored by high performance liquid chromatography (HPLC).

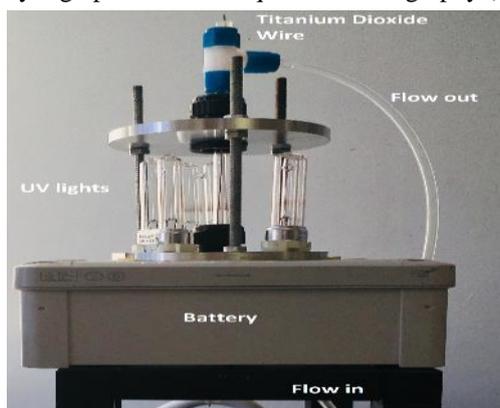


Figure 1. Tubular annular photoreactor

3. Results and Conclusion

Sodium chloride was found to be too aggressive to produce a significant oxide layer, causing severe erosion of the Ti wire. A combination of potassium bromide and ethylene glycol was found to produce a sufficient oxide layer, without leading to the dissolution of titanium wire support (shown in figure 2).

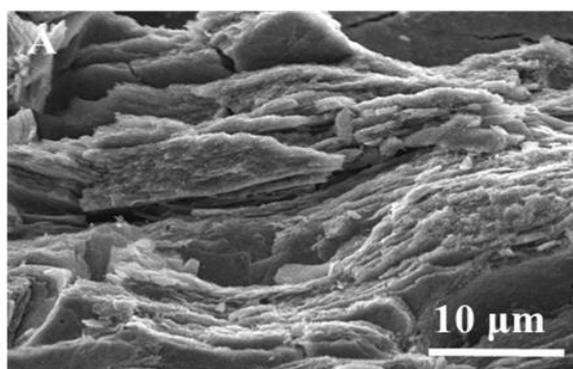


Figure 2. TiO₂ nanostructures developed from KBr anodization

The anodized TiO₂ layer produced using the KBr: ethylene glycol anodization conditions developed in this study increased photocatalytic degradation of the model pollutant, phenol (41% degradation), in comparison to an untreated Ti wire or using photolysis alone, which both degraded phenol by 25% over an hour (Figure 3).

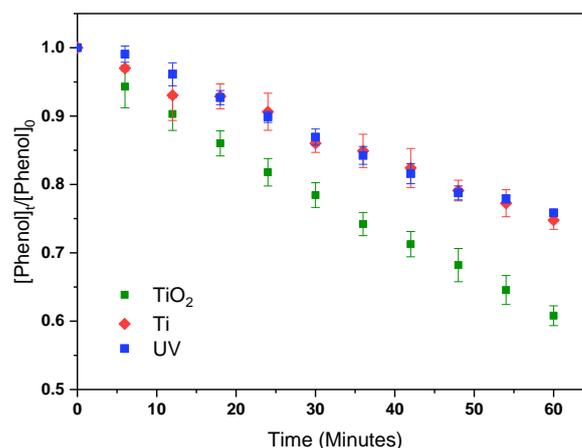


Figure 3. Photocatalytic degradation of phenol (10 μM), including error, using a untreated Ti wire, an anodized TiO₂ wire (post-annealed at 700°C) and photolysis

The bare Ti wire presents no increase in photocatalytic degradation in comparison to photolysis alone, this suggests there is no development of a natural oxide layer on the Ti surface, which is usually seen to develop for other metals such as Zn. The untreated Ti and the anodized TiO₂ wire showed good reproducibility, with a standard deviation value of ±1.33 and ±1.45 respectively. Another key parameter was found to annealing temperature, which was shown to produce the highest degradation at 700°C. This is related to the ratio of two titania crystalline phases: anatase and rutile present in the sample (determined using XRD). Annealing at 700°C, produced a ratio closest to that of TiO₂ Degussa P-25, which is commonly used as the benchmark for photocatalytic activity.

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