



Effect of duty cycle and electrolyte additive on photocatalytic performance of TiO₂-ZrO₂ composite layers prepared on CP Ti by micro arc oxidation method



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ABSTRACT

The aim of this work is to discuss the photocatalytic performance of the titania-zirconia porous photocatalyst layers synthesized via micro arc oxidation technique. An attempt was also made to put forward the basic formation mechanism of the layers. Impedance and optical properties of the photocatalyst layers were studied by electrochemical impedance spectroscopy (EIS), Photoluminescence spectroscopy and UV–vis absorption spectroscopy, in order to assess their intrinsic catalytic properties. The results of the EIS were correlated with the microstructural characteristics along with measurements of Methylene Blue (MB) photocatalytic degradation. The results show enhanced photocatalytic activity of TiO₂-ZrO₂ composite layers compared to pure TiO₂ layer. It was revealed that the photocatalytic activity of the layers prepared at different duty cycles is influenced by characteristics of microdischarge regime imposed by working electrolytes with varying additive concentration. The results of photocatalytic degradation of methylene blue were in good agreement with those obtained from electrochemical analysis.

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1. Introduction

Among the various photocatalysts, titanium dioxide (TiO₂) has received much attention due to its high photocatalytic activity, thermal stability and non-corrosive properties, biological and chemical inertness [1]. Considering the wide band gap between its valence and conduction bands, there would be a strong oxidizing power to create ·OH radicals and reduction of oxygen molecules absorption on the surface, making it a promising photocatalyst able to decompose most organic pollutants [2,3]. Nevertheless, the applications of pure TiO₂ are limited due to the high electron-hole pair recombination rate and low efficiency of visible light utilization arising from its wide band gap which means that it can be only excited under UV light wavelength. Hence, considerable efforts have been focused on increasing the ability of a photocatalytic material to overcome charge recombination and allow separated charges to interact with molecules at the surface of the material (photocatalytic efficiency). Several modifications have been employed for improving the charge separation efficiency of TiO₂ such as doping titania with noble metals [4,5], metal ions [6–8] or incorporation of other semiconductor metal oxide [9]. The incorporating metal ions into TiO₂ is considered

an efficient approach for acquiring an improved photocatalyst by introducing intermediate impurity energy levels, allowing the CB electrons to flow to noble metals and escape from recombination [10–12].

ZrO₂ is an n-type semiconductor that exhibits high ion exchange capacity and redox activities along with comparable physico-chemical properties to TiO₂. Benefitting from wide band gap (~5.0 eV) alongside conduction and valence bands with more-negative (–1.0 V vs NHE) and more-positive (4.0 V vs NHE) reducing potentials respectively, ZrO₂ is expected to be an efficient support catalyst for TiO₂ in photo-degradation application [13,14]. ZrO₂-TiO₂ binary oxide catalysts have stood out as potential materials comprehensively used in the field of heterogeneous catalysis and sensor technology due to their good optical and electronic properties and photo-stability [15,16]. Recently, it has been found that ZrO₂-TiO₂ composite photocatalysts [17,18] display enhanced photochemical properties (both in gas and aqueous solutions) than pure TiO₂ which mostly results from improved photo-generated electrons and holes separation owing to the synergistic effect of two semiconductor materials under the light function. It was also reported that the trapping of abundant OH groups on the surface of binary oxide catalyst by holes promotes the suppression of the recombination process which, in turn, improves the quantum efficiency. It is also demonstrated that incorporation of ZrO₂ in TiO₂ can promote the thermal stability of the catalyst by preventing the phase transformation from anatase to rutile [19–21].

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Typically, ZrO₂-TiO₂ composites have been synthesized via different methods including co-precipitation, sol-gel process, evaporation-induced self-assembly, and microwave-assisted solution combustion method. Micro arc oxidation (MAO) method is an economic, environmentally benign and one-step process with short working time. During MAO process discharge channels formed by electrical sparks with local temperature and pressure reaching 10³ to 10⁴ K and 10² to 10³ MPa, respectively, give rise to plasma thermochemical interactions between the substrate and the electrolyte species and let the amorphous TiO₂ transform into its crystalline form without the need for any additional heat treatment step which is required in other electrochemical methods. There are a few researches reporting the growth of photocatalyst layers by MAO method. He et al. prepared TiO₂-WO₃ photo-catalysts layers incorporated with fluorine ions [22]. Bayati et al. synthesized nano-structured TiO₂-WO₃ and TiO₂-V₂O₅ composite and pure TiO₂ layers by MAO process and studied effect of electrical parameters on their photocatalytic performance [23–25]. Very recently, Stojadinovic et al. produced Al₂O₃-ZnO, TiO₂-WO₃ and TiO₂:Eu³⁺ photocatalyst layers and probed their photocatalytic properties with increasing MAO time [26–28].

In our previous study, we characterized surface morphology and evaluated the long-term corrosion behavior of the Zr-containing layers fabricated on titanium by micro arc oxidation method [29]. In the present work, the dependence of the catalytic performance of the TiO₂-ZrO₂ composite layers on duty cycle and additive concentration are discussed in detail in order to provide vital information for synthesizing efficient photocatalytic composite layers in degradation of hazardous aqueous compounds.

2. Experimental procedure

2.1. Sample preparation

The disk specimens of commercially pure titanium (CP-grade 2) with working area of ~7 cm² were cut from a sheet with 0.8 mm thickness. For metallographic characterization, the specimens were grounded to a 1200 grit SiC finish, using water as a lubricant, degreased in ethanol, and dried in warm air. The specimens connected to the positive pole of the power supply were encircled by a hollow coil pipe made of ASTM 316 stainless steel through which cold water was run for cooling the solution. The electrolyte itself was agitated by a mechanical stirrer. The specimens then MAO-treated for 7 min in an electrolytic solution containing sodium dihydrogen phosphate (NaH₂PO₄) in 1 l of distilled water as the base electrolyte and sodium zirconate (Na₂ZrO₃) and sodium silicate (Na₂SiO₃) as additives. The composition of the electrolyte systems with their respective conductivity and pH values can be found in Table 1. The conductivity of the electrolytes was measured by MC226 basic conductivity meter (Mettler-Toledo). The micro arc oxidation process was carried out using a pulsed DC electrical power source at a fixed voltage of 500 V. The MAO process was conducted at three duty cycles viz. 30%, 50% and 70%, with a fixed frequency of 1000 Hz. The pure titania and composite layers were named TC-D and TZC-D, respectively; where C is the electrolyte code and D is the duty cycle of process.

Table 1

The composition, pH and conductivity of the electrolyte systems used for PEO process with their respective identification codes.

Electrolyte code	Electrolyte composition (g/l)	pH	Conductivity κ (mS/cm)
A0	2 g NaH ₂ PO ₄	6.1	8.7
A2	2 g NaH ₂ PO ₄ + 2 g Na ₂ ZrO ₃ + 1 g Na ₂ SiO ₃	7.2	11.4
A4	2 g NaH ₂ PO ₄ + 4 g Na ₂ ZrO ₃ + 1 g Na ₂ SiO ₃	8.6	13.1

2.2. Characterization of MAO layer

The field emission scanning electron microscopy (ZEISS SIGMA VP) with an accelerating voltage of 15.0 kV was used to study the morphology of the layers. The FE-SEM was coupled with energy dispersive spectroscopy (EDS) to assess elemental composition of the synthesized layers. The phase composition of layers was identified using a Philips X'Pert-Pro X-ray diffractometer with Cu Kα radiation (λ = 1.54060 Å). The behavior of different TiO₂-ZrO₂ layers was also studied by Electrochemical impedance spectroscopy (EIS). The EIS measurements were conducted using a Solartron 1260 model frequency response analyzer with an AC amplitude of 10 mV around OCP over the frequency range of 0.1–10⁵ Hz. The collection and evaluation of EIS data and curve fitting via circuit modeling were implemented using ZView® software. Photoluminescence (PL) spectra was measured on a Horiba Jobin-Yvon spectrophotometer under the excitation of 325 nm emission line from a Cd-He laser.

2.3. Photocatalytic experiments

The photocatalytic activity of the prepared composite layers was evaluated by photocatalytic degradation of aqueous methylene blue (MB) solution under UV irradiation. Samples of 2 cm × 1 cm, as catalysts, were immersed into 50 ml aqueous methylene blue solution (10 mg/l) in the cylindrical quartz cell with the size of 30 mm in diameter and 100 mm in height. The UV light was irradiated from a 30 W UV lamp with a maximum UV irradiation peak of 365 nm perpendicular to the surface of the layer through the sidewall of quartz cell. The distance between the layer and the lamp was 7 cm. The light intensity was measured as 1.6 mW cm⁻² using a radiometer (UV(A)-254, Lutron Electronic) attached to the outer wall of the quartz cell. Prior to irradiation, the solution and the samples were left in dark for 30 min to ensure establishment of the adsorption/desorption equilibrium. During the UV irradiation, a fixed quantity of the solution was taken out at certain time intervals to measure the absorption and the concentration. The absorptivity measurements were conducted by recording UV-vis spectra of MB using a PerkinElmer UV-vis spectrophotometer.

3. Results and discussion

3.1. Morphology, chemical and phase composition of MAO layers

Fig. 1 displays the SEM micrographs of the surface morphology of the layers produced at different duty cycles in electrolytes with various additive concentration. All the layers show porous microstructure with crater-like pores representing a typical characteristic of MAO layers. The average pore size of the layers increases with duty cycle at a constant concentration of sodium zirconate. While we can identify pores with sizes of <0.5 μm in all the layers, the largest pore size increases from ~3.6 μm to ~7.4 μm in diameter as the duty cycle increases from 30% to 70%. For the layers prepared at D = 30% and 70%, nearly 80% of the pores have a size <0.5 μm, which are actually independent of duty cycle. It can be concluded that the main effect of duty cycle on layer morphology is involved in enlarging of small-number pores. At duty cycle of 30%, the 2 g/l additive leads to an increase in layer porosity, but when the additive concentration increases to 4 g/l the layer surface becomes much more uniform with much less number of small-size pores (region "a"). By duty cycle of 70%, the pore size increases significantly with additive concentration. In fact, increasing additive concentration causes a change from a dense population of pores to smaller population of large-size pores uniformly distributed on the surface of the layers. The increasing trend of pore size with increasing additive concentration can be attributed to the decrease of electrolyte electrical resistivity when utilizing higher concentrated electrolytes. With decreased electrolyte resistivity, more energetic electric avalanches occur, which results in intensified microdischarges taking place in the

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