



Influence of atmospheric plasma spraying on the solar photoelectro-catalytic properties of TiO₂ coatings

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ABSTRACT

Titanium dioxide is a widely available material which possesses outstanding properties, chemical stability and low cost. This paper reports the synthesis of nine TiO₂ coating from three commercial TiO₂ rutile and anatase and TiO_{2-x} sub-oxide powders onto Inconel alloy substrates by means of atmospheric plasma spray (APS). The influence of this thermally-activating technique on TiO₂ powder feedstocks, the role of its spraying conditions as well as the importance of the final active behavior of the coatings were studied. The performance of the coatings as photoanodes in the solar photoelectrocatalysis (SPEC) treatment of a model azo dye was explored. APS spraying parameters were selected in order to achieve a well-bonded coating, a determined thickness and a specific surface roughness. Moreover, Argon feeding gas of plasma torch played an important role in the quick melting process, particularly related to the heat transferred to the TiO₂ particles and the achievement of non-stoichiometric TiO₂. The prepared coatings were coupled to an air-diffusion cathode inside a photoelectrochemical cell and directly exposed to sunlight irradiation. Through XRD, SEM and surface characterization of the different coatings, the properties of the best TiO₂ material for the dye degradation by SPEC were elucidated.

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1. Introduction

Titanium dioxide (TiO₂) is one of the materials of the next future due to their mechanic characteristics, biocompatibility and high stability and photocatalytic properties [1]. Taking advantage of such photocatalytic properties, TiO₂ can be employed in a wide spectrum of different advanced functional material applications such as auto-cleanable surfaces or decontamination devices to improve environmental quality [1–3]. The photocatalytic properties of TiO₂ are related to its semiconductor condition. When TiO₂ is irradiated with UV light, the transition of an electron from the filled valence band to the empty conduction band is promoted by Reaction (1), with an energy band gap of 3.2 eV, generating highly oxidative holes (h_{vb}⁺) and reductive electrons (e_{cb}⁻) [1,4]. The holes thus formed can react with water either from air humidity or from an aque-

ous media generating hydroxyl radical (*OH) from Reaction (2), the second most oxidizing species known after fluorine [3–5].



However, the photocatalytic activity is strongly lost due to the fast recombination of electrons promoted to the valence band either with unreacted holes by Reaction (3), returning to the ground state [4,5].



It is known that the specific area of TiO₂ irradiated plays an important role on its photocatalytic efficiency. A higher area allows a major promotion of Reaction (1) to compensate the efficiency lost by Reaction (3) and hence, TiO₂ nanoparticles present better photocatalytic performances than bigger shapes [1,6]. Despite this advantage, the problematic manipulation of TiO₂ nanoparticles along with their possible health hazardous effects [7,8], and the difficult recovery after usage [9,10] have avoided the application of these functional photocatalytic materials [2]. Supporting

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the nanoparticles onto substrates has been proposed as a possible solution to the aforementioned handicap [11–13]. However, the considerable diminution of exposed area to UV illumination owing to the formation of nanoparticles conglomerates mined the photocatalytic efficiency of the resulting coating [14,15].

During the last years, photoelectrocatalysis (PEC) has been considered a valuable advanced oxidation process (AOP) to solve the nanoparticles handicaps and the loss in photocatalytic efficiency of easily operable surfaces of TiO₂ such as thin-films [16–21], nanotubes [22–26], or coral structures [27,28]. The application of either a constant bias anodic potential [17,22] or a low constant anodic current density (j_{anod}) [19,29] to the TiO₂ subjected to UV illumination in PEC allows extracting the photoinduced electrons by an external electrical circuit, thus inhibiting the recombination Reaction (3) and consequently, improving the photocatalytic performance [16,29,30]. Nevertheless, to homogenize the electric distribution onto the TiO₂ surface, it is highly recommended the use of a conductive substrate like a metal in contact with TiO₂. The preparation of stable TiO₂ coatings by affordable technologies is the last challenge to overcome [17,19,21,29]. In this context, atmospheric plasma spray (APS) is a technique that produces highly stable coatings, particle by particle from molten, semi-molten or solid particles onto a substrate. Previous studies have shown that it possesses ability enough to coat large areas in short manufacturing time with an excellent specific surface layer, which is expected to improve the photocatalytic performance of TiO₂ [31,32]. The control of the synthesis parameters in APS is fundamental since they directly affect the surface characteristics and the phase composition of the coatings, thus allowing modulating the intrinsic properties of prepared TiO₂ [33].

The main aim of the present work is to prove the applicability of APS to obtain highly stable TiO₂ coatings with a wide range of structural characteristics for their application as photoanodes. The influence of the synthesis parameters on the photoelectrocatalytic performances of the different TiO₂ coatings was evaluated by means of the decolorization efficiency of a solution of a model azo dye like Acid Orange 7 (AO7) using natural solar light as inexpensive and renewable UV source in the so-called solar photoelectrocatalysis (SPEC) process.

2. Experimental

2.1. APS technology and TiO₂ coating

Thermal spray processes represent advanced techniques for coatings manufacturing. Inside this wide field, APS is known as particle-by-particle depositing method of molten, semi-molten or solid micrometric materials onto a substrate. The powder feedstock material to be sprayed is accelerated by means of a high energetic stream. The high temperatures (5000–20000 °C) and particles velocities (100–600 m s⁻¹) of the plasma jet permit to melt materials with a high melting point. During the permanence time of the particles in the hot zone of plasma jet, mixing and homogenization phenomena occur and facilitate the following deposition and coating build-up steps. The quality of coatings strongly depends on spraying parameters such as powder particle size distribution, velocities, stand-off distance, gas stream temperature, transferred heat, coefficient of thermal expansion, heat and mass flows. Particles deformation in-flight behavior of the sprayed particles is fundamental to achieve good bonding, desired thickness and final top surface roughness of the products.

To prepare the TiO₂ coatings, an APS A-3000 system with an F4 plasma torch was used, together with an ABB three-dimensional 3D robot. This facility permits to reach high deposition efficiencies, coat large areas of different substrates in low manufacturing

Table 1
Spraying conditions values for different samples.

Sample	Intensity [A]	Ar/H ₂ ratio	Distance [mm]
A1	400	2.9	140
A2	600	2.9	120
A3	600	3.4	100
B1	400	2.9	140
B2	600	2.9	120
B3	600	3.4	100
C1	400	2.9	140
C2	600	2.9	120
C3	600	3.4	100

time and produce specific surface active layers. Different Ar/H₂ gas mixtures were used and they influence the heat transferred to the particles during their permanence inside the plasma. The Ar/H₂ ratios were modified, together with the plasma intensity, in order to change the phase composition of the coatings.

2.2. Chemicals

TiO₂ rutile (Powder A) and anatase (Powder C) commercial powders were both supplied by Sulzer Metco, whereas TiO_{2-x} sub-oxide (Powder B) commercial powder was supplied by Starck Amperit. These nano-agglomerated powders were used as starting feedstocks to manufacture the final coatings using Inconel alloy as substrate. Table 1 summarizes the spraying conditions that were used to obtain the final TiO₂ coatings.

Pure azo dye AO7 was purchased from Acros Organics and used as received to test the photocatalytic activity of the synthesized TiO₂ coating by APS. Sodium sulfate used as background electrolyte to improve the conductivity of test solutions was of analytical grade supplied by Fluka. Synthetic dye solutions were prepared with high-purity water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C and their pH was adjusted to 7.0 with analytical grade sulfuric acid or analytical sodium hydroxide, both supplied by Merck.

2.3. SPEC tests

The photoelectrochemical reactor consisted in an undivided, open and cylindrical cell with a double jacket in which external water circulated to maintain the solution temperature at 35 °C using a Thermo Electron Corporation HAAKE DC 10 thermostat to avoid water evaporation under sunlight exposition as described in previous work [29]. These trials were carried out under vigorous stirring with a magnetic bar at 800 rpm to ensure homogenization and the transport of reactants toward/from the TiO₂ coating used as electrode. The different synthesized TiO₂ coatings were used separately as photoanodes with 5 cm² electroactive area exposed to sunlight and tilted 41° from the solution surface to better collect the direct sun rays in our laboratory of Barcelona (latitude: 41° 21'N, longitude: 2° 10'E). The cathode was a 3 cm² carbon-PTFE air-diffusion electrode supplied by E-TEK and mounted as described elsewhere [34]. This cathode was fed with air pumped at 300 mL min⁻¹ to generate H₂O₂ from Reaction (4). At the anodic current density of $j_{\text{anod}} = 1.0 \text{ mA cm}^{-2}$, 1.66 mM of H₂O₂ were detected in solution after 180 min of treatment, indifferently of the photoanode used. This concentration represents about a 60% of the 2.76 mM H₂O₂ expected for a 100% current efficiency, probably due to its oxidation to O₂ gas at the TiO₂ photoanode yielding the weaker oxidant HO₂• as intermediate from Reactions (5) and (6) [5,14]. This cathode was chosen because it prevents any possible reduction of the azo dye and its by-products [5].



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