TiO_2 nanotubes on titanium sponges as new supported photocatalysts for Cr(VI) removal

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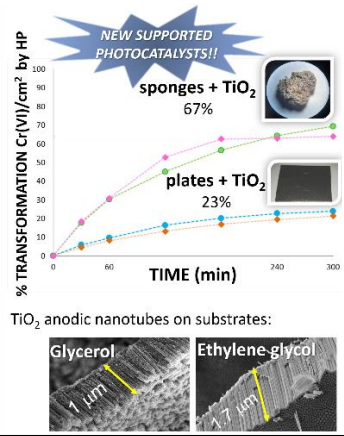

TiO_2 nanoparticles are one of the most widely used materials in heterogeneous photocatalysis for water decontamination. One of the main limitations of the development of practical systems based on this technology is the costly stage of separation and recovery of the powdered photocatalyst. A feasible solution is the synthesis of nanostructured TiO_2 coatings and one of the simplest and cheapest techniques to synthesize TiO_2 coatings is the anodic oxidation of titanium (Ti). To prevent an excessive loss of surface area due to immobilization, commercial Ti sponges with a high surface area were selected as substrates for the anodic synthesis of TiO_2 nanotubes. The coatings were characterized and their activity as photocatalysts was evaluated using Cr(VI) in the presence of EDTA. These photocatalysts are promising for their application in packed-bed photoreactors.

Introduction

Titanium dioxide (TiO_2) is the most employed semiconductor in heterogeneous photocatalysis (HP) for decontamination of water due to their low cost, low toxicity, and relatively high photocatalytic activity [1]. The HP processes usually use TiO_2 nanoparticles suspended in water, requiring an expensive further step for the separation of the nanoparticles, which can be avoided by using TiO_2 coatings [2]. One of the simplest and cheapest techniques to synthesize these coatings is the anodic oxidation of titanium (Ti), which allows obtaining oxides of diverse morphologies in different geometries [3,4]. In the present research, commercial Ti sponges with a high surface area were selected as substrates for preparation of TiO_2 coatings by anodic oxidation using fluoride ions (F^-) in glycerol and ethylene glycol-based electrolytes. This allowed obtaining long (~µm) nanotubular TiO_2 structures [3,4], which were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray microcomputed tomography. Similar coatings on Ti plates were prepared as reference. The HP activity of the coatings was evaluated by hexavalent chromium (Cr(VI)) reduction. Conventional methods of treatment of this toxic model pollutant involve expensive chemical reduction to less toxic Cr(III) species, which generates solid hazardous wastes that must be disposed. Therefore, the use of HP is a clean technology of great interest for Cr(VI) treatment. In the HP process, the reaction is accelerated by the addition of ethylenediaminetetraacetic acid (EDTA). The photocatalytic activity was determined by following spectrophotometrically the Cr(VI) concentration [3,4].

Material and Methods

Commercial titanium sponges (Sigma-Aldrich, 99.5%) with a high surface area (106 $cm^2\ g^{-1}$) were used as substrates for the anodic synthesis [5]. First, the surface were prepared by chemical pickling with $HF:HNO_3:H_2O$ 1:4:5 for 20 s. The anodic synthesis was carried out at 20 V for 2 h, using solutions with 0.27 M FNH_4 in the electrolyte in two organic media: glycerol (G) with 50% v/v water and ethylene glycol (E) with 3.5% water [3,4]. Subsequently, thermal treatments of 2 h at 450 °C were carried out with a heating rate of 10 ◦C/min and cooling inside the furnace. As reference, Ti plates (2 x 2 cm^2) were prepared, anodized and thermal treated under the same conditions.

The coatings were characterized by SEM, XRD, and X-ray microcomputed tomography.

The activity of the photocatalysts was evaluated using Cr(VI) in the presence of EDTA as a model

contaminant ([Cr(VI)] = 0.8 mM; [EDTA] = 1 mM; pH 2), irradiated with UV light (λ_{max} = 365 nm) during 5 h. Changes in Cr(VI) concentration were spectrophotometrically monitored through the diphenylcarbazide method at 540 nm (ASTM D1687–12, 2012) using a Shimadzu UV–Vis spectrophotometer, model UV-2600i.

Results and Discussion

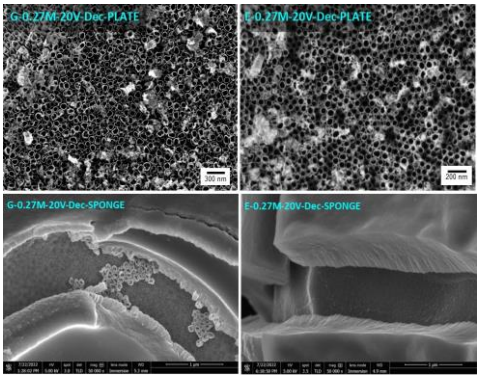

Figure 1. SEM micrographs of the coatings on plates (above) and sponges (below).

Crystalline nanotubular coatings on anatase phase (XRD spectra not shown) were obtained on the plates, with internal diameters of 40 and 50 nm, wall thicknesses of 14 and 10 nm, and lengths of 1 and 1.7 μm, with G and E electrolytes, respectively.

Nanotubular coatings were also obtained on the sponges, but with a compact TiO_2 surface layer above as it is observed in the micrographs of sponges in Figure 1 (below).

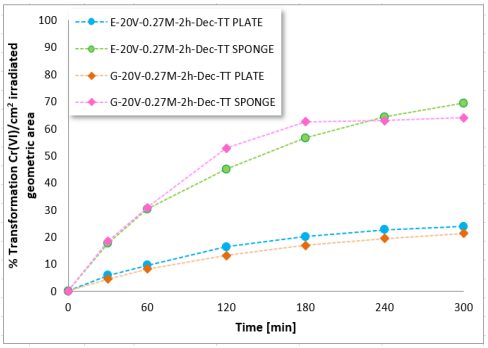

Figure 2. Evolution profiles of Cr(VI) transformation/cm^2 irradiated geometric area in photocatalytic experiments of Cr(VI) in the presence of EDTA under UV irradiation. Conditions: [Cr(VI)] = 0.8 mM, [EDTA] = 1 mM, pH 2.

Due to the porous geometry of the sponge substrate and considering the irradiated geometric area of the catalysts, sponges were much more efficient than plates, with mean 67% vs. 23% Cr(VI) transformation/cm^2 irradiated geometric area. As seen, E nanotubes rendered a better performance than G ones (at 5 h) due to higher and longer nanostructures obtained (Figure 2).

Conclusions

Crystalline nanostructured coatings were synthesized by anodic oxidation on Ti sponges and plates as substrates. Due to the porous geometry of the sponges and considering the irradiated geometric area of the catalysts, sponges were more efficient than plates, with mean 67% vs. 23% Cr(VI) transformation/cm^2 irradiated geometric area. Ethylene glycol-grown (E) nanotubes rendered a better performance than the glycerol-grown (G) ones due to higher and longer nanostructures. TiO_2 photocatalysts synthesized on Ti sponges are promising for application in packed-bed photoreactors.

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