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Correlation between photoelectrochemical behaviour and photoelectrocatalytic activity and scaling-up of P25-TiO_2 electrodes

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ABSTRACT

The use of TiO_2 electrodes may solve the two main drawbacks of photocatalytic processes: i) the necessity of recovering the catalyst and ii) the low quantum yield in the use of the radiation. This work focuses on the correlation between the photoelectrochemical properties of TiO_2 electrodes and their activity for the photoelectrocatalytic oxidation of methanol. Particulate TiO_2 electrodes prepared by deposition of P25-TiO_2 nanoparticles on titanium (TiO_2/Ti) or conductive glass support (TiO_2/ITO) seem to be effective for charge carrier transference on TiO_2 surface favouring the formation of $^{\bullet}$OH radicals and consequently, the oxidation of molecules. In contrast, thermal TiO_2 electrodes prepared by annealing of titanium (Ti) present better properties for charge carrier separation as a consequence of the application of a potential bias. Despite reducing charge carrier recombination by applying an electric potential bias, the activity of thermal electrodes remains lower than that of P25-particulate electrodes. TiO_2 structure of P25-particulate electrodes does not completely allow developing a potential gradient. However, their adequate TiO_2 layer characteristics for charge carrier transfer lead to a reduction in charge carrier recombination making up for the lack of charge carrier separation when applying an electric potential bias. TiO_2/Ti showed the highest values of activity. Therefore, the combination of the suitable TiO_2 surface properties for charge carrier transfer with an adequate conductive support seems to increase the properties of the electrode for allowing charge carrier separation. The scaling-up calculations for a TiO_2/ITO electrode do lead to good estimations of the activity and photocurrent of larger electrodes since this photoanode made from ITO as conductive support does not seem to be significantly affected by the applied potential bias.

1. Introduction

Advanced Oxidation Processes (AOPs) have been long studied for the treatment of wastewater [1]. Among them, TiO_2 heterogeneous photocatalysis, based on the generation of hydroxyl radicals upon irradiation of the catalyst with UVA light, has shown to be really effective for the degradation of many chemical pollutants [2]. This technology provides some advantages over other AOPs such as working under ambient conditions of temperature and pressure, and without additional chemical reagents. However, it has several drawbacks that hinder its massive commercialization, mainly due to the required separation of the catalyst after the treatment and the low quantum efficiency in the use of the absorbed radiation for hydroxyl radical generation due to the recombination of the photogenerated charge carriers on the semiconductor particles. One of the proposed solutions for both problems is the immobilisation of TiO_2 onto a conductive support and the application of a small potential bias between this photocatalytic electrode and a counter electrode. Under illumination, the holes migrate to the semiconductor-electrolyte interface where the water oxidation occurs, producing hydroxyl radicals, and the electrons are led to the back of the conductive support by the positive potential towards the cathode where the oxygen reduction takes place. The spatial separation of both reactions reduces the charge-carrier recombination, increasing the quantum efficiency of the process.

This *Electric Field Enhancement* (EFE) has been reported to improve the photocatalytic efficiency for degradation of organic pollutants. Since the first results reported by Vinodgopal et al. [3] and Kim and Anderson [4], several research groups have reported increasing efficiencies in the photoelectrocatalytic oxidation of several organic compounds [5]. However, some aspects of the application of photoelectrocatalytic processes for water treatment

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purposes remain still unclarified. Firstly, the efficiency of the photoelectrocatalytic processes is quite dependent on the electrode type (conductive material and TiO_2 structure) [6,7]. Thus, the efficiency of each photoelectrode might be different depending on the kind of pollutant to be removed. Secondly, oxidation activity given by a photoelectrode has been usually extrapolated from the photocurrent or electron flow registered from the anode to the cathode during the photoelectrochemical characterization of the photoelectrodes; although some authors have reported certain discrepancies in that correlation [8]. Finally, possible commercial applications requires carrying out the scaling-up of photoelectrodes to be used in a photoelectrocatalytic reactor instead of in a small electrochemical cell, where the photoelectrochemical behaviour of the photoelectrodes is usually studied. Some authors have pointed out the differences observed in efficiency or parameters such as potential bias that should be modified when photoelectrodes are scaled up [7,9].

Therefore, the aim of this work is to investigate the correlation between the electrochemical characterization of different TiO_2 electrodes and their photoelectrocatalytic activity, evaluating if the ratio between the photocurrent and photoelectrocatalytic activity of photoelectrodes is kept constant after being scaled up.

2. Experimental

Photoelectrocatalytic experiments were carried out in the stirred three-electrode electrochemical cell whose diameter corresponds to 8.5 cm. Three different 5 × 5 cm TiO_2 working electrodes (WE) were prepared: a thermal TiO_2/Ti electrode prepared by annealing a titanium foil with a resistance of $1.1 \cdot 10^{-3}\ \Omega\ sq^{-1}$ (Goodfellow) at 700 °C for 30 min following a heating rate of $50\ ^\circ C\ min^{-1}$ (sample identified as Ti) and two P25-particulate TiO_2 electrodes prepared by dip-coating in a suspension of AEROXIDE® TiO_2 P25 (Evonik Industries AG) on different conductive supports, such as titanium foil (samples identified as TiO_2/Ti) and conductive glass (coated with Indium Tin Oxide, ITO) with a resistance of $10\ \Omega\ sq^{-1}$ (Diamond coatings) (samples identified as TiO_2/ITO). Both types of dip-coated samples were annealed at 450 °C for 120 min following a heating rate of $5\ ^\circ C\ min^{-1}$. This process was repeated up to three times if not otherwise stated. More details of the dip-coating procedure can be found elsewhere [10]. Electrical contact to the conductive support was made by the attachment of a titanium wire using silver conductive epoxy resin and insulation with epoxy resin glue. A nickel mesh (55% open area) (Goodfellow), placed 1 cm over the working electrode, was used as the counter electrode (CE), being both electrodes placed on a specially designed PTFE cassette. Experiments were carried out using a total working volume of 0.4 L under stirring. The WE received front illumination by four Philips TL 6 W black light lamps with a maximum emission peak centred at 365 nm. The UV-A incident photon flow, determined by ferrioxalate actinometry, was 2.9×10^{-7} Einstein s^{-1} ($0.70\ W\ m^{-2}$). Electrochemical characterization was carried out by cyclic voltammetry (CV) at a sweep rate of $50\ mV\ s^{-1}$, once verified that differences in the results obtained at this sweep rate are negligible in comparison with those recorded at lower values of $10\ mV\ s^{-1}$. Amperometric measurements were recorded during the photoelectrocatalytic reactions at +1 V of potential bias, if not otherwise specified, using an Eco-Chemie μAutolab Type III potentiostat and a Ag/AgCl reference electrode (Bas Inc.). A two-electrode configuration of the cell (without reference electrode) was also used for scaling-up calculations. The recorded photocurrents values were transformed into photocurrent densities by considering the irradiated or photoactive surface of the electrodes ($25\ cm^2$).

TiO_2/ITO electrodes were scaled up to a cylindrical two-electrode photocatalytic reactor (Fig. 1), which consists of an annular reactor 15 cm long, 3 cm inner-tube diameter and 5 cm external-tube diameter operating in a closed recirculating circuit driven by a centrifugal pump, with a stirred reservoir tank. Experiments were carried out using a total working volume of 1 L. TiO_2/ITO electrodes whose geometric area correspond to $141.4\ cm^2$ where placed as the inner-tube. Insulated Cu wire was glued onto both extremes of the photoelectrode as detailed above. The counter electrode was a nickel mesh placed surrounding and facing the working electrode. Both electrodes were kept separated a distance of 0.5 cm by Teflon® spacers attached to the external-tube by epoxy resin glue. The illumination, provided by a Philips TL 6 W black light lamp placed in the axis of the reactor, came from the backside of the WE. The UV-A incident photon flow, determined by ferrioxalate actinometry, was 1.0×10^{-6} Einstein s^{-1} ($0.47\ W\ m^{-2}$). A potential bias was applied using as power supply the same potentiostat described above in a two-electrode configuration.

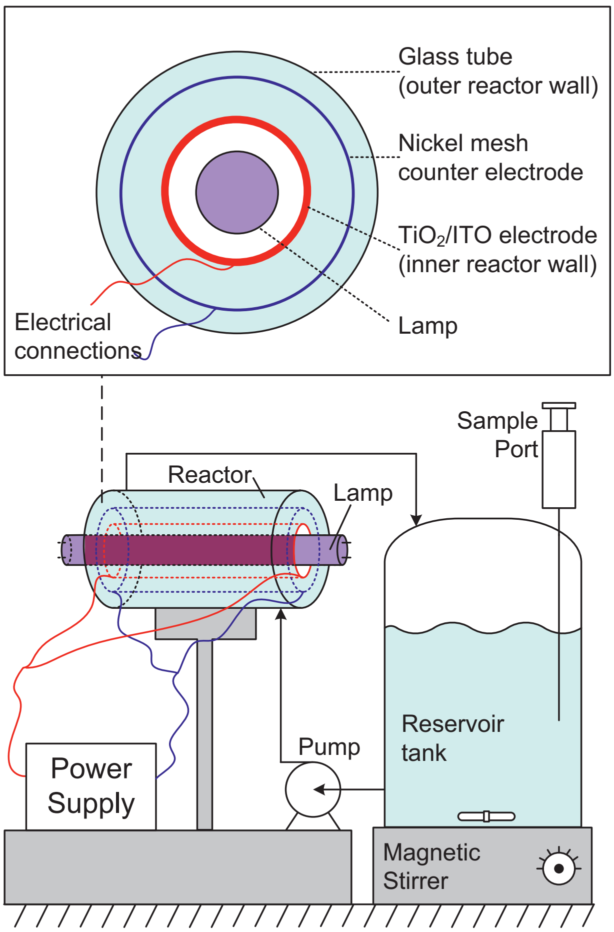

Fig. 1. Schematic representation of the experimental photoelectrocatalytic reactor (see text for details).

Methanol was chosen as model chemical pollutant to carry out one-hour experiments of photoelectrocatalytic degradation at initial concentrations of 0.01, 0.1 and 1 M, using 0.1 M Na_2SO_4 as supporting electrolyte. The evolution of the reaction was followed through the colorimetric determination of the formaldehyde produced along the reaction following the Nash's method [11]. Despite Villareal et al. [12] suggested that the final product of the oxidation of methanol corresponds to CO_2, being formaldehyde one of the intermediates, according to Sun and Bolton [13], the presence of methanol in excess leads to a quantitative production of formaldehyde.