Applied Catalysis A: General 521 (2016) 220–226

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Photocatalytic activity of one step flame-made fluorine doped TiO_2

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ARTICLE INFO

Article history:
Received 16 September 2015
Received in revised form 28 October 2015
Accepted 30 October 2015
Available online 4 November 2015

Keywords:
Photocatalysis
Flame spray pyrolysis
Fluorinated TiO_2
Oxidation reactions
Photocurrent measurements
Incident photons to current efficiency

ABSTRACT

The photocatalytic performance of a series of fluorinated TiO_2 samples (F for O molar substitution ranging from 0 to 1.5 at.%) synthesized by flame spray pyrolysis (FSP) in single step is examined in relation to the results of several complementary characterization techniques, including BET, XRD, XPS and UV–vis analyses. While the rate of photocatalytic hydroxyl radicals production increased when the photocatalyst contained small amounts of fluorine, the rate of formic acid mineralization was maximum with flame-made pure TiO_2, showing an activity even better than that of P25 TiO_2 in experiments performed in the presence of the same photocatalyst amount. However, the reaction rate decreased with increasing the nominal fluorine content of the materials, as expected for reactions occurring by direct interaction of the substrate with photoproduced holes. On the other hand, incident photon to current efficiency measurements evidenced that the presence of fluorine in the photocatalyst is beneficial, 0.29 at.% effective F for O substitution in TiO_2 leading to the best performing photocatalyst powder, in line with previous results obtained in photocatalytic hydrogen production from methanol steam reforming with similarly FSP-prepared TiO_2-based materials also containing platinum nanoparticles.

1. Introduction

The design and synthesis of cost effective, efficient and scalable materials able to convert light into chemical energy through photocatalytic processes is a key challenge for a sustainable energy economy [1]. Among the nanostructured metal oxide semiconductors suitable for this application, titanium dioxide still remains the most employed and most investigated photocatalyst [2–4], mainly because of its outstanding photostability, together with its relatively good absorption and photoproduced charge separation properties. A wide variety of synthetic routes has been developed to prepare it in different forms and shapes, with different surface area and porosity, and to improve its photocatalytic performance [5], either by enhancing its light absorption ability [6–8] or by improving the separation of the charge couples produced in it upon light absorption [9,10].

One of the strategies pursued to improve the photocatalytic performance of TiO_2 consists in fluorination, implying either surface modification (fluoride anions adsorption) or lattice fluorine doping. Surface fluorination consists in a simple ligand exchange reaction between fluoride anions and surface hydroxyl groups, which produces drastic changes in both the surface properties and the photoactivity of titanium dioxide, which largely depends also on the reaction substrate [11–16]. On the other hand, doping occurs when fluorine participates to the crystallization process of TiO_2 and leads to its modification in terms of phase, size, crystallinity, shape and exposed facets, also tuning the crystal organization into peculiar architectures and pore structures [17–22].

Surface fluorination largely depends on the properties of the pristine TiO_2 material, remarkable photoactivity changes having been observed in the case of P25 TiO_2, while much smaller effects were obtained in the case of high surface area anatase [23]. On the other hand, the increase in photoactivity induced by F-doping in TiO_2 materials prepared by sol–gel synthesis has to be essentially related to the stabilization of the highly active anatase phase up to relatively high calcination temperature and to the consequent high crystallinity of the materials [24,25]. Furthermore, intriguing synergistic effects were recently evidenced upon simultaneous bulk fluorine addition and surface modification by noble metal nanoparticles deposition of TiO_2-based materials employed in hydrogen production from water–methanol vapor mixtures [26].

Such reaction provides a way to convert solar into chemical energy at room temperature and under atmospheric pressure, with a much lower CO_2 net production in comparison to the use of fossil

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http://dx.doi.org/10.1016/j.apcata.2015.10.048
0926-860X/

fuels. Previous studies evidenced that among different TiO_2 based photocatalysts [27], best performing in this reaction are those prepared by flame spray pyrolysis in one step [28,29]. By this technique TiO_2 powders with controlled physical properties (e.g., specific surface area, crystallite size and composition) may be obtained, which guarantee good performance in both organics mineralization [30–33] and photocatalytic H_2 evolution [34,35]. In particular, a recent investigation carried out employing a series of fluorinated Pt/TiO_2 photocatalysts evidenced that 5 at.% F for O substitution in TiO_2 was optimal for achieving high H_2 production rate through this reaction [36].

In the present work, we try to elucidate the origin of the better performance of fluorinated flame-made TiO_2 materials containing different amounts of fluorine, in a systematic investigation aimed at correlating their photoactivity, in both powder and film form, with their surface and bulk properties.

2. Experimental

2.1. Photocatalysts preparation

A series of fluorine-doped TiO_2 samples was synthesized in continuous and single step by flame spray pyrolysis [28,29,37]. These samples were labeled as FSP_*x* with *x* corresponding to the nominal F/O percent molar ratio, ranging from 1.0 to 10%. The precursor organic solution was prepared by dissolving 18.3 mL of titanium(IV)-isopropoxide in a 10 vol.% propionic acid in xylene solution (total volume 100 mL). Hexafluorobenzene, added in different volumes ranging from 23 to 233 μL, was employed as fluorine source.

The so-obtained liquid organic solutions were fed to the burner at 4 mL min^{-1} by the syringe pump through the capillary tube placed at the center of the vertical nozzle [36] and dispersed by oxygen (5 L min^{-1}) at 2 bar constant pressure drop across the burner nozzle. The produced powders (yield ≈50%) were collected on a glass fiber filter (Whatman GF/A, 26 cm in diameter) placed on top of a cylindrical steel vessel surmounting the flame reactor and connected to a vacuum pump (Busch Seco SV 1040C).

All chemicals employed in the synthesis of the materials and in the preparation of all solutions were purchased from Aldrich. Water purified by a Milli-Q water system (Millipore) was used throughout.

2.2. Photocatalysts characterization

X-ray powder diffraction (XRPD) patterns were recorded on a Philips PW3020 powder diffractometer, by using the Cu Kα radiation (λ = 1.54056 Å). Quantitative phase analysis was made by the Rietveld refinement method [38], using the "Quanto" software. The average anatase crystallite size was calculated according to the Scherrer equation, from the integral XRD peak width calculated as the ratio between the peak area and peak intensity obtained by fitting with a Gaussian function the profile of the most intense reflection at $2\theta = 25.4°$.

Diffuse reflectance (*R*) spectra of the photocatalyst powders were recorded on a Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere, using barium sulphate as a reference, and then converted into absorption (*A*) spectra ($A = 1-R$). The BET specific surface area (SSA) was measured by N_2 adsorption at liquid nitrogen temperature (77 K) on a ASAP 2020 apparatus, after out-gassing in vacuo at 150 °C for at least 2 h.

X-ray photoemission spectroscopy (XPS) data were collected by a PHI-5500—Physical Electronics spectrometer, equipped with an aluminium anode (Kα = 1486.6 eV) as monochromatized source, operating at a 200 W of applied power, 58.7 eV pass energy and 0.5 eV energy step. The analysis area is around 0.5 mm^2 and the sampling depth is within 10 nm. During measurements the vacuum level was around 10^{-9} Torr. In order to neutralize the surface electrostatic charge of nonconductive samples an electron gun was used. Furthermore, the charging effect on the analysis was also corrected considering the binding energy (BE) value of C(1s), due to adventitious carbon, at 285.0 eV. The quantitative analysis data were reported as atomic percentage of elements; the normalization was performed without including hydrogen.

2.3. Preparation of titania films

The home-made FSP_*x* nanopowders were deposited on FTO transparent electrodes by the following procedure. A TCO22-7 FTO glass was first cut in the appropriate size (1.5 cm × 1.0 cm) and carefully cleaned by sonication for 30 min first in distilled water and then in a 1:1 acetone-isopropyl alcohol solution. The electrodes were then dried in oven at 70 °C for 2 h and calcined at 500 °C for 4 h.

The conductive layer of the FTO glass was coated with a paste containing the FSP_*x* samples and spin coated in a Laurell WS-650MZ-23NPPB spin coater at 600 rpm for 180 s. The paste was obtained by mixing 60 mg of fluorine-doped TiO_2 powder with 0.5 mL of ethanol and 0.02 mL of acetic acid, followed by sonication for about 90 min. Then 0.4 mL of ethanol were further added to the paste, which was stirred overnight before being deposited and spin coated on FTO. The FTO-coated films were then calcined at 300 °C for 3 h, with a heating ramp of 10 °C min^{-1}. Their thickness was 720 nm ± 120 nm, as determined by a DeltaXT profilometer. The area of each film was carefully fixed at 1.0 cm^2 (1.0 cm × 1.0 cm).

2.4. Photoactivity tests

2.4.1. Photocatalytic decomposition of formic acid

All photocatalytic formic acid (FA) degradation runs were performed under atmospheric conditions in a magnetically stirred 60 mL cylindrical quartz reactor, inserted in a home made housing consisting of a black box mounted on an optical bench [24]. The irradiation source was an Osram, model Powerstar HCI-T, 150 W/NDL lamp, mounted on a Twin Beam T 150 R reflector, mainly emitting at λ > 340 nm. The light intensity on the reactor in the 300–400 nm range was 5×10^{-8} Einstein s^{-1}, as calculated from the emission spectrum of the lamp and its full emission intensity, which was regularly checked with an optical power meter.

The irradiated aqueous suspensions always contained 0.1 g L^{-1} of photocatalyst and a FA initial concentration equal to 1.0×10^{-3} mol L^{-1}. After preliminary ultrasound treatment for 30 min, the suspension was magnetically stirred in the dark for 15 min to attain the adsorption equilibrium of the substrate on the photocatalyst surface, before starting irradiation. Stirring was continued during the photocatalytic runs. 2 mL-samples of the suspension were withdrawn from the photoreactor at different time intervals during the runs and centrifuged employing an EBA-20 Hettich centrifuge. The supernatant was analysed for residual FA content by ion chromatography with conductivity detection, employing a Metrohm 761Compact IC instrument, after calibration for formate ion concentration in the 0–50 ppm range. During FA degradation the pH of the suspensions increased, from initial values around 3.7 to ca. 4.8, as a consequence of FA mineralization to CO_2 and H_2O.

2.4.2. Terephthalic acid photocatalytic oxidation

The same photoreactor and setup were employed to test the efficiency of the prepared photocatalysts in the oxidation of terephthalic acid (benzene 1,4-dicarboxylic acid), following the procedure described in Ref. [39]. 10 mg of each photocatalyst were first dispersed in 54 mL of ultrapure water by 30 min-long sonication.