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Photocatalytic hydrogen production over flame spray pyrolysis-synthesised TiO_2 and Au/TiO_2

Gian Luca Chiarello, Elena Selli *, Lucio Forni

Dipartimento di Chimica Fisica ed Elettrochimica, CIMAINA and ISTM-CNR, Università degli Studi di Milano, via Golgi 19, I-20133 Milano, Italy

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ABSTRACT

A set of titanium dioxide and gold-modified titanium dioxide samples were prepared by flame spray pyrolysis (FP) and characterized by BET, XRD, HRTEM and UV–vis reflectance analysis. Their photocatalytic activity in hydrogen production in water suspension, either from water photosplitting or from methanol photoreforming, was tested in an expressly set up, closed recirculation laboratory scale photoreactor and compared to those of commercial TiO_2 samples, including Degussa P25, pure rutile and pure anatase. The rate of hydrogen evolution (r_{H_2}) increased with increasing the anatase content, pure anatase being the most active photocatalyst. Surface area and crystallinity, both key properties of photocatalysts, can be tuned up by properly setting FP operation parameters, including the selection of the organic solvent/fuel. In particular, FP-made TiO_2 prepared from a xylene solution showed more active than P25. Finally, r_{H_2} increased by one order of magnitude in water photosplitting and by *ca.* 30 times in methanol photoreforming upon 1% gold addition on TiO_2.

1. Introduction

The photocatalytic hydrogen production using solar energy is a challenging research topic which has received much attention in recent years for its potential to provide H_2 as a clean and renewable energy resource even on a large scale [1]. This can be attained mainly by two processes, *i.e.* either by the direct splitting of water into hydrogen and oxygen [2], or by the photoreforming of organic compounds [2–5]. The latter process, occurring in the absence of oxygen, is very attractive especially when polluted wastewater is used as feed-stock, two goals being obtained in this case: the abatement of organic pollutants together with the production of hydrogen, an energy carrier.

In the last decade, different mixed metal oxides semiconductor photocatalysts, also with rather complex structure, such as layered or differently doped perovskite-based materials, have been proposed for water photosplitting [6–9]. However, titanium dioxide still remains the most suitable photocatalyst, in consideration of its high activity, chemical inertness, low cost and non toxicity [2,10].

Photocatalytic reactions on semiconductors are initiated by the absorption of a photon with energy equal to, or greater than, the semiconductor bandgap. This promotes an electron from the valence band (VB) to the conduction band (CB), with the consequent formation of an electron (e^-_{CB})–hole (h^+_{VB}) pair. The so produced charge carriers can induce the reduction of electron acceptor species and the oxidation of electron donor species, respectively, both adsorbed on the semiconductor surface. In the case of water cleavage, the electron acceptor would be the H^+ ion and the electron donor would be H_2O, according to the following reactions:

$$TiO_2 + 2h\nu \rightarrow 2e^-_{CB} + 2h^+_{VB} \quad (1)$$

$$2H^+ + 2e^-_{CB} \rightarrow H_2 \quad (2)$$

$$H_2O + 2h^+_{VB} \rightarrow \tfrac{1}{2}O_2 + 2H^+ \quad (3)$$

The overall photocatalytic water splitting formal reaction is, therefore:

$$H_2O + 2h\nu \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (4)$$

Presently, one of the major problems in the exploitation of photocatalytic hydrogen production via water splitting over semiconductors is the low quantum efficiency of the process, consequent to the high probability of photogenerated electron–hole pairs recombination, releasing energy in the form of unproductive heat. Many efforts have been done in the last decades to increase the activity of semiconductor metal oxides,

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* Corresponding author. Tel.: +39 2 503 14237; fax: +39 2 503 14300.
E-mail address: elena.selli@unimi.it (E. Selli).

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Table 1
Combustion enthalpy (ΔH_c) of the solvents employed in FP synthesis; specific surface area (SSA), from BET analysis, phase composition and crystallite dimensions, from XRD analysis, of the investigated TiO_2 photocatalysts

Sample	Solvent/fuel	ΔH_c (kJ cm^{-3})	SSA (m^2 g^{-1})	Anatase		Rutile	
				wt%	d_A (nm)	wt%	d_R (nm)
FP1	Propionic acid	−20.6	66	56	27	44	37
FP2	2-Ethylhexanoic acid	−30.1	59	40	19	60	26
FP3	Propionic acid/methanol 2/8	−18.3	68	56	21	44	33
FP4	Xylene	−37.4	54	66	21	34	32
FP5	Xylene/pyridine 8/2	−36.7	106	90	11	10	8.6
Au/FP5	Xylene/pyridine 8/2	−36.7	106	90	10	10	9.0
P25	–	–	48	81	19	19	28
Anatase	–	–	285	100	5.6	0	–
Rutile	–	–	12	0	–	100	44

e.g. by adding "sacrificial agents" able to efficiently combine with e^-_{CB} or h^+_{VB}, or by modifying the photocatalysts by noble metal loading, to favour charge carriers separation.

Methanol and other organic species may act as sacrificial agents in photocatalysis, being able to combine with photogenerated valence band holes more efficiently than water (see reaction (3)). Thus, conduction band electrons become more readily available for reduction reactions, *e.g.* hydrogen production from water (reaction (2)). The presence of noble metal nanoparticles on the surface of semiconductor metal oxides can increase the electron–hole pair separation, because photopromoted electrons can be "captured" by the noble metal, if its Fermi level is lower in energy than the CB potential [2]. As electrons accumulate into the noble metal particle, their Fermi level shifts to more negative values, closer to the CB level of TiO_2, this upward shift being more negative, the smaller is the metal particles size [11]. Thus, H^+ ions reduction to H_2 over the noble metal surface is easier and more efficient than over TiO_2. Fig. 1 shows a schematic representation of the mechanism of photocatalytic water splitting over Au/TiO_2.

In the present work the photocatalytic activity in hydrogen production from water photosplitting of a series of TiO_2 samples prepared by flame spray pyrolysis has been investigated, as well as the effect of both the addition of methanol and the deposition of gold nanoparticles on titanium dioxide.

Flame spray pyrolysis (FP) proved to be an effective method for the synthesis of nanosized TiO_2 and noble metal-modified TiO_2, yielding high surface area, crystallinity, anatase content and better noble metal dispersion [12–15]. Furthermore, a FP-synthesised TiO_2 photocatalyst was recently shown [15] to be more active than Degussa P25 in the photomineralisation of saccharides.

A FP apparatus for the preparation of different mixed oxides has been recently set up by our research group and the influence of the operation parameters on the properties of a series of FP-synthesised perovskite catalysts have been investigated in detail [16–19]. In the present work the FP synthesis of TiO_2 has been optimised, focusing in particular on the effects that the organic solvent nature and operation conditions may have on the physicochemical properties of the produced powders and on their photocatalytic activity in water splitting and methanol reforming.

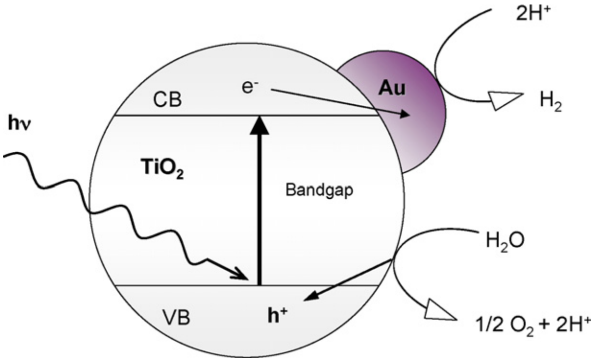

Fig. 1. Schematic representation of the mechanism of water photocleavage over Au/TiO_2 semiconductor particles.

2. Experimental

2.1. Photocatalysts preparation

The TiO_2-based photocatalysts FP1–FP5 (Table 1) were synthesised by the FP method, starting from a solution prepared by dissolving titanium(IV)-isopropoxide (Fluka, purum), 0.15 M, in different organic solvents and employing the home-made apparatus fully described in ref. [16]. The liquid solution was fed at 3.1 mL min^{-1} in the flame reactor and dispersed by oxygen (6 L min^{-1}) at 1.5 bar constant pressure drop across the nozzle (internal diameter, 1.5 mm). Samples FP5 and Au/TiO_2, this latter containing 1% gold nanoparticles, were synthesised at the Institute of Chemical and Bioengineering of ETH, Zurich, employing the flame pyrolysis apparatus and operation conditions described in ref. [14]. In the case of Au/TiO_2, the desired amount of gold precursor (dimethyl-gold(III)-acetylacetonate, >99%, Strem) was dissolved in pure xylene, together with the Ti-precursor. Another 1% Au/TiO_2 sample (Au/P25) was prepared via deposition of *tetrakis*(hydroxymethyl) phosphonium chloride-stabilised gold nanoparticles on Degussa P25 TiO_2, as detailed elsewhere [20].

Degussa P25, together with a pure anatase (Millennium Chemicals) and a pure rutile (Tioxide) sample, was also investigated, for comparison.

2.2. Characterization methods

XRD measurements were performed on a Philips PW3020 powder diffractometer, by using the Cu Kα radiation ($\lambda = 1.54056$ Å). The diffractograms were compared with literature data [21] for phase recognition. Quantitative phase analysis was made by the Rietveld refinement method [22–24], using the "Quanto" software [25]. The average size of the crystallites was obtained by the Scherrer equation. The most intense reflection peak of each phase (at $2\theta = 25.4°$ for anatase and at $2\theta = 27.5°$ for rutile) was fitted with a Gaussian function to obtain the integral breadth of the reflection.

The BET surface area was measured by N_2 adsorption/desorption at 77 K on a Micromeritics ASAP 2010 apparatus, after out-gassing in vacuo at 300 °C for at least 6 h. For high-resolution and scanning transmission electron microscopy (HRTEM), the material was dispersed in ethanol and deposited onto a perforated carbon foil, supported on a copper grid. The analysis was done on a