Applied Catalysis B: Environmental 163 (2015) 452–458

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Photocatalytic hydrogen production on Pt-loaded TiO_2 inverse opals

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ARTICLE INFO

Article history:
Received 22 May 2014
Received in revised form 1 August 2014
Accepted 19 August 2014
Available online 24 August 2014

Keywords:
TiO_2
Inverse opal
Hydrogen production
Slow light
Slow photons

ABSTRACT

TiO_2 inverse opals present increased photocatalytic production of H_2. TiO_2 inverse opals with different pore size and TiO_2 macroporous structures with disordered arrangement of the pores have been tested in the photocatalytic production of hydrogen in aqueous solution with a formate buffer as hole scavenger. TiO_2 inverse opals belong to the family of metamaterials and exhibit unique catalytic properties arising from their peculiar interaction with light. To discriminate the effects of slow photons the hydrogen photoproduction experiments were carried out at two different wavelengths, at 365 nm where the effect of slow photons is maximized, and at 254 nm where it is negligible. The resulting hydrogen production rates suggest a strong effect of the slow light and of the polymer template used in the synthesis of the TiO_2 powders. The chemical properties of the polymeric sacrificial template determine the crystalline phase of the sample and as a consequence affect the catalytic performances of the resulting TiO_2 structures.

1. Introduction

Photonic crystals are materials in which the refractive index varies periodically in the space, and, since light can be refracted and reflected at each interface, for a wavelength matching the lattice periodicity there is the possibility to have constructive interference of the reflected waves. At that wavelength light is completely reflected and cannot propagate inside the material because of the presence of the photonic band gap (PBG) [1,2]. Owing to this, photonic crystals find applications as dielectric mirrors [3–6], waveguides [7], lasing cavities [8,9], and black body radiation modifiers [10]. At the PBG edges light can propagate inside the photonic crystal, but its group velocity is strongly reduced, and thus its interaction with the material increases, opening the field to a series of diversified applications [11,12].

The increased light-matter interaction can be exploited in photocatalysis. Recently Tsai et al. published an interesting report [13] on the interaction of light with hierarchical structured TiO_2, specifically hollow spheres, which could harvest more light thanks to the scattering effect in the microstructure while maintaining high surface area. Among photonic crystals TiO_2 inverse opals (TIOs) have been studied extensively to improve the efficiency of the photocatalytic process [14–16]. TIOs are constituted of ordered arrays of holes in a TiO_2 matrix, but they only possess a partial PBG, because the refractive index of TiO_2 is not high enough to open an omnidirectional gap [17]. Previous results show that TIOs can significantly increment the photocatalytic performances of TiO_2 thanks to the slow light phenomenon, which is the improved light-matter interaction due to the reduction of the group velocity of light at the PBG edges [18–21]. In a previous work [21] we have clarified that besides slow photons, porosity and specific surface area give only a negligible contribute to the observed increase in photocatalytic activity of these structures. The photoelectrochemical study of such materials [22] showed that TIOs and disordered macroporous TiO_2 structures share the same recombination rate of the photogenerated charge carriers, but TIOs are characterized by a faster electron transfer to the oxygen present in solution. After our early analysis, other research works observed that the slow photon effect markedly improved the photocatalytic activity in the oxidation of dyes [23], and increased three times the performance of Bi_2WO_6 deposited on SiO_2 photonic crystal compared to ordinary Bi_2WO_6 films [24]. The slow photon effect was also responsible for the enhanced photodegradation of the AO7 dye on TIOs doped with Ti^{3+} [25]. Conversely, the porous structure plays an important role in electrocatalytic reactions [26]. Thus the enhanced absorption of light, the improved reactivity towards oxygen and, to a lesser extent, the improved mass transfer of substrates make TIOs good candidates as catalysts for photo-reduction reactions.

To test the presence of a synergic effect between slow light and faster electron transfer to solution, in the present work we have compared the activity of Pt-loaded TIOs and of Pt-loaded

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Abbreviations: PBG, photonic band gap; TIO, TiO_2 inverse opal; MP, macroporous; XRD, X-ray diffraction; PMMA, polymethylmethacrylate; PS, polystyrene.

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http://dx.doi.org/10.1016/j.apcatb.2014.08.028
0926-3373/

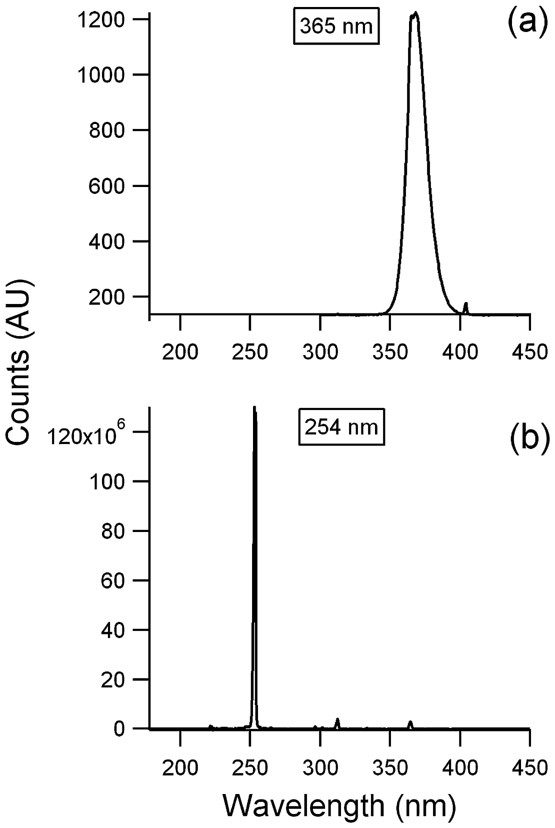

Fig. 1. Emission spectra of a Philips TUV PL-S lamp (a) and of a Philips PLS-10 lamp (b).

macroporous disordered TiO_2 structures in hydrogen photoproduction experiments. To detect the effect of slow photons we performed irradiations at two different wavelengths: at 365 nm, where the TIOs synthesized can take advantage of slow light, and at 254 nm, where for the TIOs considered the slow light contribution to the photocatalytic activity is negligible. The hydrogen production rates of TIO samples are then compared with those of disordered macroporous samples.

2. Experimental

2.1. General

TiO_2 P25 was a gift of Degussa, methyl methacrylate (MMA, 99%), styrene (99%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (97%), titanium (IV) isopropoxide (97%), hexachloroplatinic acid hexahydrate (37.5% Pt basis), formic acid (85% in water), ethanol (99.9%) and ethylene dimethacrylate (98%), were purchased from Aldrich, sodium formate (99%) from Merck. All the products were used without further purification.

2.2. Powder preparation

TIOs and TiO_2 macroporous structures were synthetized using different polymeric sacrificial templates. Polymethylmethacrylate (PMMA) and polystyrene (PS) templates were used to obtain TiO_2 structures with different pore sizes. The detailed synthesis procedure has been described elsewhere [21], here we only summarize the relevant issues. PMMA syntheses were carried out following a modified method proposed by Waterhouse and Waterland [27], in which the stirring procedure was changed [21]. With vigorous mechanical stirring well monodisperse colloids were produced, whereas with magnetic stirring polydisperse colloids were obtained.

Table 1
Specific surface area, diameter of the macropores and TiO_2 crystalline phases present in the TiO_2 powders synthesized (A: anatase, B: brookite, R: rutile).

Sample	SSA ($m^2 g^{-1}$)	Macropore size (nm)	Crystalline phases
TIO-PMMA	18	125	Anatase, rutile < 1%
MP-PMMA	28	200–220	Anatase, rutile ≈ 2%
TIO-PS	74	330	A ≈ 57%, B ≈ 36%, R ≈ 7%
MP-PS	69	300–330	A ≈ 70%, R ≈ 30%
P25	45 [46]	–	A ≈ 80%, R ≈ 20% [47]

Monodisperse polystyrene (PS) spheres were prepared with emulsion polymerization without emulsifier with a modified version of the method proposed by Goodwin et al. [28]. The size of the PS spheres produced is highly dependent on the composition of the synthesis mixture and on the reaction temperature, while the monodispersity of nanoparticles strongly depends on the stirring of the reaction mixture. To obtain well monodisperse colloids we carried out syntheses with mechanical stirring. Polystyrene polydisperse colloids were obtained mixing various batches of monodisperse colloids.

Polymer colloid size and polydispersity were measured with an ALV-NIBS High Performance Particle Sizer (ALV GmbH). Polymeric colloidal suspensions were diluted approximately from 5 to 100-fold with Milli Q water before measurements and the particle size was extrapolated at infinite dilution.

Opals made with monodisperse polymer particles and polymeric disordered structures have been prepared loading PMMA or PS colloidal suspensions into 50 mL plastic falcon tubes followed by centrifugation (4300 rpm, 15 °C for 90 min). The supernatant was then removed, and the polymeric disordered structure or the polymeric colloidal crystal was left to dry in air at 25 °C for 24 h.

Macroporous TiO_2 (MP) and TIOs were prepared filling the interstices among polymer spheres in polymeric disordered structures and polymeric opals with a TiO_2 precursor. 1.5 g of the polymer template were gently crushed with a metal spatula to give fractured pieces of size <2 mm, which were then deposited on a filter paper (Whatman, Qualitative 1, 11 μm) placed into a sintered glass filter funnel (Millipore). With a strong vacuum applied to the sintered glass filter funnel, a solution of TiO_2 precursor (4 mL titanium (IV) isopropoxide and 4 mL ethanol) was poured drop wise over the surface of the polymeric structure. Infiltrated samples were then left to dry in air at 25 °C for 2 h and recovered. Polymeric templates were then removed by means of calcination in air using the following protocol: the temperature was raised from 25 to 300 °C at 2 °C min^{-1}, held at 300 °C for 5 h, then raised again from 300 to 550 °C at 2 °C min^{-1}, held at 550 °C for 12 h. Samples were then finally allowed to cool to room temperature over 3–4 h.

On the as prepared materials, Pt was photocatalytically reduced adding H_2PtCl_6 to catalyst slurries and irradiating with UV light (see below).

2.3. X-ray powder diffraction

X-ray powder diffraction (XRD) patterns have been recorded with a PW3050/60 X'Pert PRO MPD diffractometer from PANalytical working in Bragg-Brentano configuration. The X-ray source was a high power ceramic tube PW3373/10 LFF with a Cu anode and the instrument was equipped with a Ni filter to attenuate K_β. Diffracted photons were collected with a real time multiple strip X'celerator detector. Powder samples have been hosted on SiO_2 amorphous sample holder.

The relative amounts of the different TiO_2 polymorphs were assessed with the method proposed by Zhang and Banfield [29].