



Dynamic photocatalytic hydrogen production from ethanol–water mixtures in an optical fiber honeycomb reactor loaded with Au/TiO₂



Elena Taboada^a, Inma Angurell^b, Jordi Llorca^{a,*}

^a Institut de Tècniques Energètiques and Centre for Research in NanoEngineering, Universitat Politècnica de Catalunya, Av. Diagonal 647, Ed. ETSEIB, 08028 Barcelona, Spain

^b Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

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ABSTRACT

Cordierite honeycombs loaded with different amounts of Au/TiO₂ have been used in an optical fiber photoreactor illuminated with UV LEDs to produce hydrogen from ethanol and water–ethanol mixtures. The photoreactions have been carried out at 298–348 K, volume hourly space velocities of 300–2100 h⁻¹, Au contents of 0.5–2 wt.% with respect to TiO₂, and ethanol molar contents of 1–100%. Excellent dispersion and homogeneous particle size of gold has been obtained by using pre-formed, dendrimer-encapsulated Au nanoparticles. The best photocatalytic performance has been obtained over monoliths loaded with ca. 0.5 mg cm⁻² of Au/TiO₂ (1.0–1.5 wt.% Au), which corresponds to a photocatalyst layer thickness of about 1 μm. In gas phase, acetaldehyde adsorption onto the photocatalyst surface plays an important role in the dynamics of the photoprocess by affecting hydrogen evolution sites, which is improved with temperature and short contact times. Hydrogen photogeneration in liquid phase is significantly enhanced (fivefold increase) in the optical fiber honeycomb photoreactor with respect to a conventional slurry photoreactor.

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1. Introduction

There have been intensive efforts toward the development of technologies for the sustainable production of hydrogen from renewable resources, mainly water and biomass, to boost the use of hydrogen as energy carrier for meeting future fuel needs with no carbon footprint [1]. These include steam reforming of biomass components [2,3], water splitting [4,5], and dark fermentation [6] routes. Photocatalytic H₂ production over irradiated semiconductors is receiving particular attention because of based on the Sun, which is a perpetual source of energy, and it is an environmentally safe technology without undesirable byproducts. Initially, electron–hole pairs are generated in semiconductors upon bandgap excitation. Depending on the excitation lifetime relative to that of charge recombination, a net fraction of photocharges are present, which are trapped at defect sites or migrate toward the photocatalyst surface. These surface electrons and holes can reduce and oxidize surface adsorbed molecules, respectively. The structural and electronic properties of semiconductor photocatalysts largely determine the photocatalytic H₂ production and numerous nanostructures and hybrid assemblies have been proposed [7–9]. TiO₂-based photocatalysts are among the most attractive due to their availability, corrosion resistance, non-toxicity, low price and high photoactivity and stability. The biggest disadvantage of TiO₂

is the low utilization of visible light, as a consequence of its wide bandgap.

Incorporating organics such as carboxylic acids, alcohols and carbohydrates as sacrificial electron donors into the photocatalytic process increase charge-separation efficiency and give higher H₂ generation rates [10,11]. The rate of hydrogen evolution is much higher, compared to that obtained in the absence of organics in the irradiated photocatalyst, due to the irreversible oxidation of the organic molecule with photogenerated holes and the concomitant suppression of electron–hole recombination and H₂–O₂ back reaction, which are the most important processes for decreasing the light-to-hydrogen conversion efficiency. Among the most promising hole scavengers is ethanol because it is readily available, easy to obtain from biomass (bioethanol) and to transport, CO₂-neutral and safe to handle [2].

The effect of the addition of noble metal nanoparticles (the so-called cocatalyst) to TiO₂ is well known as it considerably increases the hydrogen production rate. Deposition of Au nanoparticles onto TiO₂ has been found to enhance hydrogen production by facilitating electron transfer and therefore inhibiting electron–hole recombination as well as by reducing the overpotentials for H₂ generation [11–13]. Au/TiO₂ has also the ability to increase the photoresponse of TiO₂ to visible light because of the Au surface plasmon band at 500–600 nm (localized surface plasmon resonance effect, LSPR). Au nanoparticle size, dispersion, loading, and metal–support interaction all play critical roles in determining the photocatalytic activity of Au/TiO₂ with all these parameters

* Corresponding author. Fax: +34 93 401 71 49.

E-mail address: jordi.llerca@upc.edu (J. Llorca).

depending on the catalyst preparation methods [14,15]. Another important parameter is the polymorphism of the TiO₂ support; for Au loaded onto rutile, hydrogen production is about two orders of magnitude lower than that on anatase due to the greater charge recombination rate of rutile as compared to anatase [16]. On the contrary, support particle size is not an important parameter for Au/TiO₂ photocatalysis [17].

It is important to stress out that, whereas material development constitutes an active area of research, it represents only one of the key elements of a photocatalytic system [18]. Designing a functional photocatalytic system for practical application requires an integrated approach involving engineering photon delivery in proper photoreactors as well as optimum mass transfer. No matter how active a photocatalyst, if photons are not effectively transmitted to its surface then its full potential will not be reached and system efficiency will be lowered. For instance, slurry photoreactors, which are the most used in photocatalysis research, facilitate mass transfer, but they are limited by poor light penetration in the suspension (the irradiance of light decreases inversely with the square of distance from the source). The major parameter that is currently assessed with respect to illumination is the amount of illuminated surface per unit of volume inside the reactor, but this parameter does not take into account other aspects related to illumination, such as the ratio incident/emitted light power and the uniformity of light incidence [18]. In many photoreactor designs (slurry reactors, annular reactors, spinning disk reactors, optical tube reactors and immersion reactors), the light has to travel through the fluid or gas containing reagents and also through a transparent wall. In addition, it is very difficult to achieve uniform irradiance on the entire catalyst surface, which is critical because a minimum energy level is needed to activate the photocatalyst. Once the photocatalyst is activated, maximized contact between the photocatalyst and reagents should be achieved, as well as the removal of the reaction products formed. An ideally intensified photoreactor should be able to integrate both maximized light efficiency and mass transfer simultaneously. One of the main developments in improving illumination efficiency has been the introduction of optical fibers [19–21]. In an optical fiber reactor, the photocatalyst is typically coated on the fibers, where light is propagated along the fiber length by reflection on the fiber wall. However, one problem is that light intensity decays exponentially along the axial direction of the coated fiber and that the amount of refraction in the fiber depends on the thickness of the photocatalyst coating. Another problem with coated optical fibers is that the charge carriers (electrons and holes) are generated far from the interface between the photocatalyst and the reagents (because of the back-irradiation) and, consequently, are more susceptible to recombination loss. Recently, a substantial improvement has been reached in the field of water/air treatment by designing optical fiber honeycomb reactors, where the photocatalyst is immobilized on the monolith wall [22–24]. With this configuration, high light efficiency and availability combined with optimum mass transfer and scale-up potential can be achieved.

In this work, the dynamic hydrogen production from water–ethanol mixtures is investigated in an optical fiber reactor over Au/TiO₂ immobilized on ceramic monoliths. Several operational parameters have been studied, such as photocatalyst loading on the monolith wall, water–ethanol ratio, temperature, residence time, and gaseous vs. liquid feed. In order to avoid undesirable effects originating from catalyst preparation we have used dendrimer-protected pre-formed Au nanoparticles to ensure a constant Au nanoparticle size [25] and to prevent Au agglomeration [26]. The influence of Au loading on hydrogen photoproduction has also been explored.

2. Experimental section

2.1. Photocatalyst preparation

Cordierite (Al₄Mg₂Si₅O₁₈) honeycombs (Rauschert, 100 cells per square inch, pore volume 210 ± 30 mm³ g⁻¹, average pore diameter 3 ± 1.5 μm) measuring 16 mm in diameter and 20 mm length were obtained by cutting larger pieces with a diamond saw. They contained exactly 21 square channels with 2.1 mm channel width. The photocatalyst used was Au/TiO₂ and the preparation of the photocatalytic monoliths involved two steps. First, the honeycombs were coated with a pure TiO₂ layer by soaking them into pure titanium isopropoxide, Ti(OCH(CH₃)₂)₄. Different TiO₂ loadings were achieved by blowing with dry air the titania precursor. Honeycombs were then dried under continuous rotation for 30 min at room temperature followed by 30 min at 393 K. Finally, they were calcined at 723 K for 4 h (10 K min⁻¹). Titania mass was monitored by weight gain and ranged from ca. 5 to 100 mg.

Gold nanoparticles were loaded onto the TiO₂ layer by incipient wetness impregnation from a toluene solution containing pre-formed Au nanoparticles measuring ca. 2.5 nm and capped with thiol-derived carboxilane dendrons HS(CH₂)₃Si((CH₂)₃-Si(CH₃)₃)₃, which were prepared as reported previously [25]. The Au loading was varied between 0.5 and 2 wt.% with respect to TiO₂. Honeycombs were finally calcined at 673 K for 2 h (2 K min⁻¹) to eliminate the carboxilane dendron shell and to assure a tight contact between the Au nanoparticles and the TiO₂ support. This temperature was selected following a detailed in situ XPS and HRTEM study reported in [27]. After calcination the monoliths exhibited the characteristic purple color of Au/TiO₂ containing small Au nanoparticles, with the purple coloration intensifying with Au loading.

2.2. Photocatalyst characterization

The photocatalytic Au/TiO₂ cordierite honeycombs were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) and focus ion beam (FIB), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), UV–Vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). SEM–EDX–FIB was carried out with a Zeiss NEON40 crossbeam instrument. XRD patterns were collected between 10° and 90° of 2θ with a step width of 0.02° and a step time of 1 s using a Bruker D8 instrument equipped with Cu Kα incident radiation and a graphite monochromator. HRTEM was carried out with a JEOL J2010F electron microscope equipped with a field emission gun operating at an accelerating voltage of 200 kV. Samples were dispersed in alcohol in an ultrasonic bath, and a drop of supernatant suspension was poured onto a holey carbon coated grid. UV–Vis reflectance spectra were collected with a Shimadzu UV3600 UV–Vis–NIR spectrometer equipped with an integrating sphere. XPS was performed on a SPECS system equipped with an Al anode XR50 source operating at 200 mW and a Phoibos 150 MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Charge stabilization was achieved by using a SPECS Flood Gun FG 15/40. The binding energy (BE) values were referred to the C 1s peak at 284.8 eV. Surface area measurements (BET) of the TiO₂ powders were carried out with a Micromeritics ASAP 2000 apparatus after degassing at 443 K. Temperature-programmed desorption (TPD–MS) was conducted in a Catalyst Analyzer Belcat–M instrument coupled to a Cirrus MKS mass spectrometer equipped with a multiplier detector.

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