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Silicone microreactors for the photocatalytic generation of hydrogen

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ABSTRACT

A silicone microreactor with 500 μm-width microchannels coated with a Au/TiO_2 photocatalyst was manufactured and tested for the photocatalytic generation of hydrogen from gaseous water-ethanol mixtures under dynamic conditions. The manufacture of the microreactor included the fabrication of a polylactic acid (PLA) mold with a 3D printer and casting with polydimethylsiloxane (PDMS) prepolymer. After curing, the silicone microreactor was peeled off and the microchannels were coated with a Au/TiO_2 photocatalyst prepared by impregnation of preformed Au nanoparticles over TiO_2, and sealed with a thin silicone cover. The microreactor was tested at room temperature and atmospheric pressure under different operational conditions (photon irradiance, residence time, photocatalyst loading, and water-ethanol ratio). Hydrogen production rates of 5.4 NmL W^{-1} h^{-1} were measured at a residence time of 0.35 s using a H_2O:C_2H_5OH molar ratio of 9:1, a photocatalyst load of 1.2 mg cm^{-2} and a UV irradiance (365 nm) of 1.5 mW cm^{-2} achieving an apparent quantum efficiency of 9.2%. The photogeneration of hydrogen with commercial bioethanol was also tested. A long-term photocatalytic test of two days revealed a stable hydrogen photoproduction rate. The use of silicone microreactors represents an attractive and customizable solution for conducting photochemical reactions for producing hydrogen at low cost.

1. Introduction

Heterogeneous photocatalysis is a well-known catalytic process with many applications in water treatment and air purification [1,2]. Recently, it has also been proposed as an interesting route for the production of renewable hydrogen from water and organic compounds for energy applications [3,4], which has boosted a renewed interest in the formulation of photocatalysts as well as in the development of new photocatalytic reactor concepts. Semiconductor photocatalysis has received much attention over the past few decades as a promising solution to capture and convert the energy supplied by the Sun (light) into chemical energy stored in the H—H bond. Among the various semiconductor photocatalysts tested so far, TiO_2-based systems (anatase or rutile-anatase mixtures) seem to be the most promising, due to their availability, high chemical stability, non-toxicity and low cost. Unfortunately, TiO_2 is inefficient for hydrogen generation due to low activity as a consequence of its wide bandgap (3.0–3.2 eV), so it is necessary to modify the surface of TiO_2 to enhance its photon efficiency (apparent quantum yield). This can be done by decorating the TiO_2 particles with metal nanoparticles that can accept the photoexcited electrons from the conduction band of the semiconductor, and/or by adding sacrificial agents that are oxidized by the holes created in the valence band. Ethanol is considered an excellent hole scavenger because it is readily available, easy to obtain from biomass, and safe to handle [3].

It is important to recall that the success of photocatalytic hydrogen production will be affected not only by the activity of the photocatalyst itself, but also by the effective transmission of photons to its surface. Most of the photocatalytic processes reported so far use agitated slurry reactors, which suffer from poor photon transfer from the external photon source to the photocatalyst particles in suspension. In addition, the photocatalyst particles must be recovered downstream using centrifuges and filters. Several solutions have been proposed to overcome the photon transfer limitations without sacrificing mass transport, such as the use of optical fibers inside photocatalytic honeycombs [5–7] and conventional optofluidic devices made out of quartz or Pyrex with microchannels made by either micro-milling, etching processes or laser ablation [8,9]. In these devices, in addition to increasing reaction rates by improving both mass and optical transfer efficiencies, the photocatalyst is immobilized on the reactor walls and no recovery is necessary. Photocatalytic microreactors with immo-

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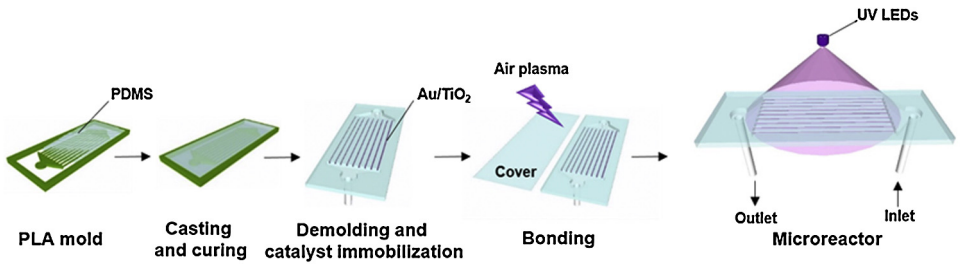

Fig. 1. Scheme of the fabrication steps of the silicone microreactors.

bilized TiO_2 catalyst have already proven to be a highly effective tool for the synthesis of fine chemicals and for the selective cleavage of peptides and proteins [10,11]. However, these solutions are expensive and difficult to implement. In this work, we report on the fabrication of silicone microreactors containing microchannels by replica molding with an immobilized Au/TiO_2 photocatalyst for producing hydrogen from water-ethanol mixtures. This method provides a rapid, cheap, and customizable manufacture of microreactors with easy scale up and rapid prototyping for the continuous photoproduction of hydrogen.

2. Experimental methods

2.1. Fabrication of the photocatalytic silicone microreactors

The silicone microreactors were fabricated by casting polydimethylsiloxane (PDMS) prepolymer over a polylactic acid (PLA) mold manufactured with a 3D printer. Fig. 1 shows a scheme of the procedure used. Google SketchUp and Slic3r software were used for the design of the PLA mold. The primary advantage of this technique is that almost any shape or geometric feature can be created. In our case, the mold consisted of nine rods of 500 μm (width) × 1 mm (depth) × 47 mm (length), with a total volume of 0.21 cm^3, and two collectors to facilitate gas distribution as shown in Fig. 1. The molds were fabricated with a replicating rapid prototyper RepRap BCN3D printer with PLA extruded at 210–220 °C. The printing time for each mold was ca. 8 min. In order to obtain the silicone microreactors, a mixture of PDMS prepolymer (elastomer) and curing agent (cross-linker) Sylgard 184 (Dow Corning) was prepared with a ratio 10:1 (w/w) and degassed. The mixture was poured onto the PLA mold and the assembly was cured at 100 °C for 45 min. After curing, the resulting silicone microreactor was peeled off from the mold and appropriate connections were inserted. The same procedure was used to fabricate the cover (thickness of ca. 400 μm), but in this case PDMS was poured on a flat glass surface. PDMS is optically transparent down to 240 nm.

The Au/TiO_2 photocatalyst was deposited on the walls of the silicone microchannels from a sonicated ethanol suspension containing the photocatalyst particles. To attain a proper immobilization, a corona discharge plasma treatment was previously applied over the microchannels to produce a silanol-terminated surface. The photocatalyst was prepared by incipient wetness impregnation of pre-formed Au nanoparticles dispersed in toluene over commercial TiO_2 (Degussa P90; ca. 90 $m^2\,g^{-1}$), with a metal loading of 1.8 wt.% with respect to TiO_2. This value was selected following previous studies, where an optimum Au loading of 1–2 wt.% was found [6,12,13]. The pre-formed Au nanoparticles consisted of metallic Au cores covered by a protective shell of dodecanethiol and were prepared as reported previously [7]. Briefly, $AuCl_4^-$ was first transferred from aqueous $HAuCl_4$ solution (40 mM) to toluene solution using tetraoctylammonium bromide as a phase transfer reagent. Dodecanethiol was then added to the solution at a 1:1 molar ratio of dodecanethiol:Au, and an excess of aqueous

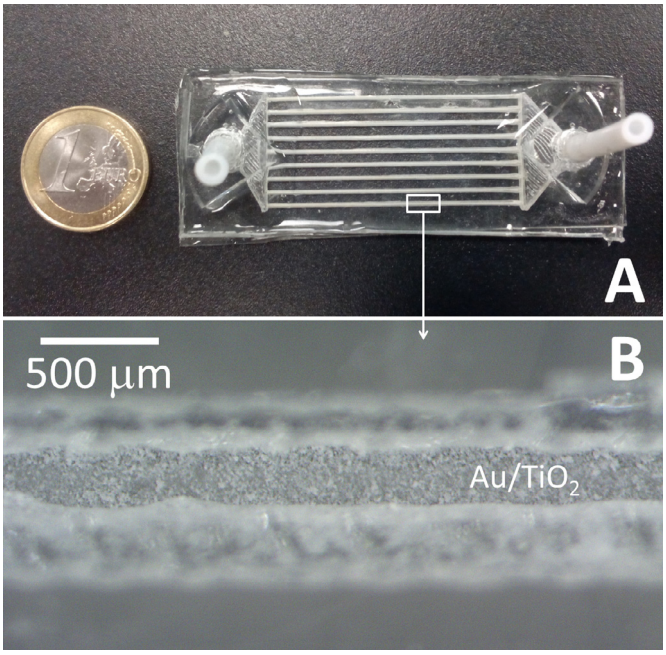

Fig. 2. Picture of a silicone microreactor loaded with photocatalyst (A) and image obtained by optical microscopy of the catalytic layer deposited over a microchannel (B).

$NaBH_4$ was slowly added to reduce the metal salt. The resulting dodecanethiol-capped metallic nanoparticles were dried and cleaned using ethanol. The photocatalyst was calcined at 673 K for 2 h (2 K min^{-1}) to eliminate the protective shell and to assure a good contact and electronic interaction between the Au nanoparticles and TiO_2 support. This temperature was selected following the study reported in [14]. No further activation was required for the photocatalytic experiments. Different photocatalyst loadings were tested, namely 0.5, 1.2, 2.4 and 7.1 mg cm^{-2} (total weight of catalyst with respect to the surface exposed by the microchannels). Finally, after immobilization of the photocatalyst over the microchannels, the silicone microreactor was sealed with the silicone cover using a corona plasma treatment (BD-20AC Electro-Technic Products) for 2 min over both pieces, which were pressed together and baked overnight at 75 °C (Fig. 2A).

2.2. Characterization

The photocatalyst was characterized by X-ray diffraction (XRD), UV–vis reflectance spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The microchannels and the deposition of the photocatalyst on their walls were observed before and after the photocatalytic test by optical microscopy. XRD measurements were carried out with a Bruker D8 diffractometer with CuKα