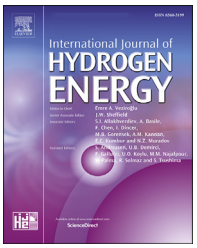
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

Available online at www.sciencedirect.com

ScienceDirect

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



Hydrogen photocatalytic production from the self-assembled films of PAH/PAA/TiO_2 supported on bacterial cellulose membranes

Nicolle Dal'Acqua [a], *Ana Claudia Rangel Faria* [a], *Mário César Vebber* [a], *Hernane da Silva Barud* [b], *Marcelo Giovanela* [a], *Giovanna Machado* [c], *Janaina da Silva Crespo* [a,*]

[a] *Área do Conhecimento de Ciências Exatas e Engenharias, Universidade de Caxias do Sul, Rua Francisco Getúlio Vargas, 1130, Caxias Do Sul, 95070-560, RS, Brazil*

[b] *Universidade de Araraquara, Uniara, Laboratório de Biopolímeros e Biomateriais (BIOPOLMAT), Rua Carlos Gomes, 1217, 14801-320, Araraquara, SP, Brazil*

[c] *Centro de Tecnologias Estratégicas do Nordeste, Av. Prof. Luiz Freire, 01, 50740-540, Recife, PE, Brazil*

ARTICLE INFO

Article history:
Received 5 April 2018
Received in revised form
21 June 2018
Accepted 28 June 2018
Available online xxx

Keywords:
Self-assembled films
Bacterial cellulose membrane
Gold nanoparticles
Hydrogen production

ABSTRACT

The issues related to renewable energy sources is a matter of great worldwide appeal due to the increasing energy demand, instability in oil prices and environmental problems. In this context, the purpose of this study was to prepare self-assembled films of polyallylamine hydrochloride and poly (acrylic acid) supported onto bacterial cellulose membranes by a layer-by-layer approach with titanium dioxide (TiO_2) nanoparticles and different concentrations of gold for application in hydrogen gas (H_2) production by photocatalysis. The influence of the gold concentration and the presence and size of the gold nanoparticles (Au NPs), as well as the surface and thickness of the films on H_2 production was investigated. The results showed that the film, prepared with a lower concentration of gold, presented the smallest Au NPs and, therefore, greater contact with the TiO_2 nanoparticle surfaces, producing more H_2. By analyzing the variation in all the experimental parameters used in the preparation of the films, it can be concluded that the best H_2 production achieved was 29.12 μmol h^{-1} cm^2.

Introduction

The concern for the preservation of the environment and the scarcity of fossil fuels has intensified the search for renewable energy sources [1,2]. Among the alternative energy sources, H_2 has received special attention because it is a clean fuel and has great potential as a future energy carrier. Currently, 95% of H_2 is produced either from wood or fossil fuels, such as natural gas and oil. Therefore, technological advances seeking environment friendly and efficient production are under development worldwide [3–5].

Among the technologies for H_2 production, one of the highlights is photocatalysis, which consists in the breakdown of water molecules into H_2 and O_2 under solar radiation using a semiconductor that transforms the energy contained in the photons into electric energy [6–8]. TiO_2, an inorganic semiconductor, has been applied in photocatalysis due to its high

* *Corresponding author.*
E-mail address: jscrespo@ucs.br (J.S. Crespo).

https://doi.org/10.1016/j.ijhydene.2018.06.176
0360-3199/

photostability and ability to be activated by sunlight. This semiconductor presents better performance when excited in the ultraviolet (UV) region, which represents only 4–5% of the solar energy reaching the Earth's surface. Ongoing research efforts have focused on the improvement of the utilization of solar radiation through an extension of the absorption region of TiO_2 from the UV to visible range with the aid of visible-light sensitizers, such as gold nanoparticles (Au NPs), which enhance photocatalytic activity in the production of H_2 [9–11].

Metallic nanoparticles on the surface of TiO_2 are able to increase the absorption of visible light due to their surface resonance plasmon, which interacts with electromagnetic radiation, absorbing photons in the visible light range. In addition, Au NPs, as well as other noble metal particles, have Fermi levels with energies lower than that of the conduction band of TiO_2; therefore, an excited photon will be transferred into the Au adsorbed on the surface of the photocatalyst. This process traps the charge carriers and reduces charge recombination, one of the main mechanisms that lowers the efficiency of TiO_2. Metal NPs loading stands out among other forms of doping because of its simplicity in terms of material development (no advanced chemical or physical deposition equipment required). Moreover, it provides two different mechanisms for increased performance, which also work on already doped samples, i.e., TiO_2 doping and metal loading are not mutually exclusive, but complementary. Recent studies have also indicated that photocatalytic efficiency is enhanced with reduced size and higher density of Au NPs, due to electrical, optical and topographical properties [6,12–15].

Another interesting way to increase the efficiency of H_2 production consists of the use of TiO_2 in nanoparticulate form. Generally, the absorption of photons in photocatalysis is interpreted as a property of volume; therefore, the contribution of the absorption of the surface layers may become important in NPs. As the diameter of the semiconductor particles decreases, the number of surface atoms considerably increases. Consequently, the photocatalytic activity increases with the decreasing size of the particles due to the larger surface area available for reaction [6].

Nowadays, studies related to photocatalytic thin films aim to improve the use of the solar radiation [16,17]. In 2013, Dal'Acqua et al. [18] produced H_2 using photocatalytic films composed of self-assembled polyelectrolytes/TiO_2/Au NPs on glass, silicon and polystyrene substrates. In another study performed by Dal'Acqua et al. [19], H_2 was produced with nanostructured films on a bacterial cellulose (BC) flexible substrate. In addition to these surveys, Faria et al. [20] and [21] studied photocatalytic H_2 production by films made of polyelectrolytes, TiO_2 and cadmium selenide NPs, and Vebber et al. [22] produced H_2 with thin films of polyelectrolytes, TiO_2 and copper chlorophyllin.

These films can be obtained, for example, by the layer-by-layer technique (LbL) using the sequential adsorption of two oppositely charged polyelectrolytes [23]. Weak polyelectrolytes are often used to produce nanostructured thin films by the LbL technique. Among those, poly (acrylic acid) (PAA) and polyallylamine hydrochloride (PAH) are arguably the ones most often described in the literature and whose properties are well characterized. Because the ionization degree of these materials depends of the pH, different film properties and behaviors can be achieved by changing the acidity or alkalinity of the medium [19–22,24,25]. Self-assembled thin films present even more interesting properties when deposited on flexible substrates, because they offer a thin and light profile, which can be easily shaped in different formats to optimize surface area, for example. This fact represents a substantial advantage over rigid substrates, such as glass, silicon or ceramics.

Many papers have proposed different types of cellulose as flexible substrates for the incorporation of semiconductors and metallic NPs [26–29]. BC is a natural polymer and has the same chemical structure of vegetal cellulose, but with fibers of nanometric dimensions. This type of material is synthesized by certain bacteria and does not contain lignin, hemicellulose or pectin, i.e., high purity cellulose, with high crystallinity (from 70 to 80%), water content above 90% and high mechanical strength. In addition, BC is a biodegradable, biocompatible, non-toxic and non-allergic polymer. Due to these chemical and structural properties, BC can be considered as an ideal hydrophilic matrix for the incorporation of inorganic and metallic NPs [30–32].

Therefore, the aim of the present work was to evaluate the influence of the gold concentration in the preparation of different films with PAH, PAA and TiO_2 supported on BC membranes. Additionally, the effect of the Au NPs size on the H_2 production was also assessed.

Experimental section

Pre-inoculum and biosynthesis of bacterial cellulose (BC) membranes

Gluconacetobacter xylinus (ATCC 23769) was maintained in Hestrin and Schramm (HS) solid culture medium at 4–8 °C. One single colony from the solid medium was used to inoculated into 50 mL of modified HS liquid medium, composed of 50.0 g L^{-1} of glucose, 4.0 g L^{-1} of yeast extract, 0.73 g L^{-1} of $MgSO_4$. $7H_2O$, 2.0 g L^{-1} of KH_2PO_4, 20.0 g L^{-1} of ethanol and distilled water (1.0 L). The set was incubated at 28 °C for 24 h in static condition.

BC membranes were produced by cultivating *Gluconacetobacter xylinus* for three days at 28 °C, under static conditions, in 500 mL Erlenmeyer flasks containing 90 mL of HS medium and 10 mL of pre-inoculum. Subsequently, BC membranes were purified by rinsing with 0.1 mol L^{-1} NaOH solution at 80 °C for 30 min. Finally, BC membranes were washed with deionized water several times until neutral pH [33].

Multilayers deposition

Firstly, the wet BC membranes were fixed on glass slides (VWR International, 7.5 cm × 2.5 cm) using elastic bands at both the top and bottom edges. The wet membranes adhere rapidly and spontaneously to slide surface; thus, this procedure was carried out in order to avoid eventual displacements. The films were prepared on the BC using two weak polyelectrolytes: a cationic polyelectrolyte (PAH, $M_w = 70{,}000$ g mol^{-1}, Sigma-Aldrich) and an anionic polyelectrolyte (PAA, $M_w = 90{,}000$ g mol^{-1}, 25 wt%, Polysciences) [34–36]. These two polyelectrolyte solutions were

Please cite this article in press as: Dal'Acqua N, et al., Hydrogen photocatalytic production from the self-assembled films of PAH/PAA/TiO_2 supported on bacterial cellulose membranes, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.06.176