INCORPORATION OF GOLD NANOPARTICLES IN MULTILAYERS OF WEAK POLYELECTROLYTES FOR HYDROGEN PRODUCTION

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EXTENDED ABSTRACT

The issues related to renewable energy sources is a matter of great worldwide appeal due to increasing energy demand, instability in oil prices and environmental problems. In this context, the self-assembled thin films have gained considerable scientific interest in numerous applications in nanotechnology, among them the construction of photovoltaic power generating systems and photoluminescent devices. In view of these facts, the goal of this work was to prepare and characterize thin films produced by layer-by-layer (LbL) technique supported in bacterial cellulose, using two weak polyelectrolytes (polyallylamine hydrochloride – PAH, and poly(acrylic acid) – PAA) supplemented with titanium dioxide (TiO₂) and gold nanoparticles, aiming to create a device for producing hydrogen. Bacterial cellulose, inorganic materials and nanostructured thin films were characterized through instrumental techniques including ultraviolet and visible (UV-Vis) absorption and Fourier transform infrared spectroscopies (FTIR) and scanning electron microscopy (SEM). In general, the HAuCl₄ and TiO₂ solutions exhibited typical absorption bands in the UV region. The FTIR spectra, on the other hand, showed the presence of characteristic functional groups of the PAA and cellulose. The SEM images revealed that the surface of bacterial cellulose presents a crosslinked structure formed by cellulose fibers. Concerning the thin films, it was observed an absorption band for the AuNPs at ~580 nm in both systems {(PAH+TiO₂)₇.₀ (1:1) / PAA₄.₀}2₁ and {(PAH+TiO₂)₄.₀ (1:1) / PAA₄.₀}₂₁. Furthermore, the {(PAH+TiO₂)₇.₀ (1:1) / PAA₄.₀}₂₁ film containing the highest amount of AuNPs presented a rate of hydrogen production of 1.96 μmol cm⁻² h⁻¹.

Keywords: gold nanoparticles, self-assembling films, bacterial cellulose.

1. INTRODUCTION

The issues related to renewable energy sources are of great worldwide appeal, mainly due to growing demand for energy, coupled with the instability of oil prices and environmental problems. Among the various renewable energy sources, solar energy has received considerable attention as an alternative to conventional energy sources due to its efficiency and clean operation, minimizing environmental pollution (Othman, 2013).

According to the report from the Energy Information Administration of the United States, the generation of renewable energy worldwide will increase from 10% in 2012 to 16% in 2035. In this context, the self-assembled thin films have gained considerable scientific interest inspiring numerous applications in nanotechnology such as the construction of photovoltaic power generating systems and photoluminescent devices (Durán, 2006).

Among the methods for manufacturing thin films, the layer-by-layer (LbL) is one the most efficient technique in the construction of nanostructured materials showing a series of advantages, including simplicity of the process and possibility of deposition at room
temperature. In general, the films are produced via sequential adsorption of polyelectrolytes from dilute aqueous solutions based on electrostatic interaction of oppositely charged polymers (Decher, 2002).

Moreover, the use of weak polyelectrolytes in LbL systems allows control of layer thickness and molecular organization of the polymer chains adsorbed by simply adjusting the pH of the solutions (Burke, 2003). In this study, we chose two polyelectrolytes: polyallylamine hydrochloride (PAH) and poly(acrylic acid) (PAA).

Between the semiconductors used as power converters, the titanium dioxide (TiO$_2$) has received special attention because it presents good chemical stability over a wide pH range, photostability and ability to activation by sunlight. This photocatalyst semiconductor is also effective when irradiated with ultraviolet light (Nogueira, 1995).

It is well known that only 4% of ultraviolet radiation coming from the sun reaching the Earth and the use of inorganic materials that absorb light in the visible region can be used to enable more efficient capture sunlight. As inorganic materials, stand out the metallic nanoparticles of silver (Ag), platinum (Pt), and gold (Au). These nanoparticles have unique optical and electronic properties, including the nanometer size that easily absorbs heat and high surface/volume ratio. For these reasons, they have been used in developing of new generation nanodevices (Kamat, 2002; Srinivasan, 2006).

The current challenge is the fabrication of thin films on flexible substrates with metallic nanoparticles. An example of a pliable substrate is the bacterial cellulose (BC) which is obtained from several genera of bacteria such as *Glucanacetobacter xylinum*. The main characteristics of BC include the crystallinity, elasticity, durability, and high absorption capacity and water retention (Donini, 2010).

In the view of these facts, the main objectives of this work was to prepare and characterize thin films of weak polyelectrolytes (PAH and PAA) supported in BC and combined with TiO$_2$ and gold nanoparticles (AuNPs) for producing flexible devices capable of producing hydrogen gas.

2. MATERIALS AND METHODS

The substrate used as support in the self-assembled thin films was the BC. Initially, the BC was washed with distilled water to remove the basic solution where it was stored. The washing was carried out until the final pH of the washing water the membranes stay at 5.5. For the preparation of thin films, the wet membrane was fixed on glass slides.

PAH ($M_w = 70,000$ g mol$^{-1}$) (Sigma-Aldrich) was used as the polycation whereas PAA ($M_w = 90,000$ g mol$^{-1}$, 25 wt%) (Polysciences) was used as the polyanion. All polyelectrolytes were prepared into 0.01 mol L$^{-1}$ solutions (based on the repeat-unit molecular weight). For the TiO$_2$ semiconductor (STS-100, $M_w = 80$ g mol$^{-1}$, 15.4 wt%) (Ishihara Sangyo Kaisha Ltd.), it was used a solution with a concentration of $0.0375$ mol L$^{-1}$.

Substrates were immersed in the polycation aqueous solution with the semiconductor aqueous solution (PAH+TiO$_2$) for 15 min followed by rinsing once for 2 min, and again for 1 min in deionized water. The substrate containing the adsorbed polycation was then dipped into the polyanion solution (PAA) for 15 min and the process was repeated. The multilayers were obtained with aqueous solutions composed of $((PAH+TiO_2)_x \times (z:w) / PAA)_i$, where $x$ is the pH of the solution of the polycation and semiconductor, $z$ and $w$ are volumetric proportions of the PAH and TiO$_2$ solutions, $y$ is the pH of the solution of the polyanion, and the $i$ is the number of layers. Finally, multilayers were prepared for two compositions: $((PAH+TiO_2)_{7.0} \times (1:1) / PAA_{4.0})_{21}$ and $((PAH+TiO_2)_{4.0} \times (1:1) / PAA_{4.0})_{21}$. 
These films were immersed in a solution of HAuCl₄ for 1 h at pH = 2.3, and then removed and rinsed in deionized water for 1 min. After incorporation of the gold salt, the films were exposed under ultraviolet radiation (UV) for 48 h at 365 nm to promote the reduction of the metal ions forming the AuNPs. Structural characterization of thin films was evaluated using ultraviolet/visible molecular absorption (UV-Vis) and Fourier transform infrared spectroscopies (FTIR), and scanning electron microscopy (SEM).

The rate of hydrogen production, on the other hand, was determined by a gas chromatograph (Agilent 6820) equipped with a thermal conductivity detector (TCD) and a 2.0 m stainless column packed with Porapak-Q (80/100 mesh). Nitrogen was used as a carrier gas.

3. RESULTS

3.1 Characterization of inorganic materials and bacterial

3.1.1 UV-Vis of TiO₂ and HAuCl₄ solutions

Molecular absorption spectra in the UV-Visible region (Figure 1) show, respectively, an absorption maximum in the region of 200-240 nm for HAuCl₄ with inflection point near the region of 220 nm, and an absorption maximum in the wavelength region below 350 nm for TiO₂. The main bands presented in these spectra are related to the fundamental electronic transitions of d electrons of gold and titanium metals.

![Figure 1. UV-Vis spectra of TiO₂ and HAuCl₄ solutions.](image)

3.1.2 FTIR of BC

The FTIR spectrum of BC is shown in Figure 2. In a general way, the spectrum presents several bands, among which may be cited: [1] the stretching of the OH groups (3342 cm⁻¹), [2] the CH stretching (2894 cm⁻¹), [3] the CH₂ deformation (1426 cm⁻¹), [4] the CH₃ deformation (1357 cm⁻¹), [5] the OH deformation (1336 cm⁻¹), and [6] the CO deformation (1055 cm⁻¹). Moreover, this spectrum presented the main bands that are indicative of the structure of cellulose and which is consistent with those presented in the literature (Qu, 2010; Barud, 2006).
Figure 2. FTIR spectrum of BC.

3.1.3 SEM of BC

The SEM image of the surface of dry BC (Figure 3a) shows the structure formed by the crosslinked cellulose fibers and Figure 3b presents these fibers in a cross section of the BC.

Figure 3. SEM of BC: (a) surface, and (b) cross section.

In general, the BC fibers are strongly associated with intramolecular (responsible for the rigidity of the chain) and intermolecular (the formation of vegetable fiber) hydrogen bonds. Among these fibers, it is also possible to observe the presence of compact pores on its surface (Figure 3a).
3.2 Characterization of the thin films

3.2.1 UV-Vis spectroscopy

Figure 4 presents the UV-Vis spectra of the thin films after exposure in UV light.

![UV-Vis spectra of thin films](image)

**Figure 4.** UV-Vis spectra of thin films.

As can be observed, there was the incorporation of the AuNPs in both systems since the spectra showed a maximum absorption at around 580 nm, which is characteristic of AuNPs (Mayya, 2003). Furthermore, the \((\text{PAH} + \text{TiO}_2)_{7.0}(1:1) / \text{PAA}_{4.0}\) system presented the highest absorbance indicating that there was a better incorporation of AuNPs in relation to the other thin film. In this case, the PAH polyelectrolyte with pH = 7.0, this means is further charged group \(–\text{NH}_3^+\) than at pH = 4.0, aiding in the incorporation of AuNPs (Rubner, 2005). As a result, we decided to apply the gas chromatography only in this thin film to evaluate the hydrogen production.

3.2.2 GC analysis

Hydrogen gas production was quantified by gas chromatography. Figure 5 shows the result of the production of H₂, in μmol of H₂ produced per cm² as a function of irradiation time for the thin film \((\text{PAH} + \text{TiO}_2)_{7.0}(1:1) / \text{PAA}_{4.0}\).

In general, the \((\text{PAH} + \text{TiO}_2)_{7.0}(1:1) / \text{PAA}_{4.0}\) showed a photocatalytic potential of 1.96 μmol cm² h⁻¹ of H₂. As this result is recent, measurements of H₂ production of self-assembled thin films only with polyelectrolytes and TiO₂ should be performed for comparison.

TiO₂ is a photocatalytic material and its light absorption occurs only in the ultraviolet region, so it becomes more efficient when combined with the visible light sensitizers, such as AuNPs. Because of this, studies are being conducted to determine a better distribution of TiO₂ and AuNPs in the films aiming an increase of the photocatalytic potential.
**Figure 5.** \( H_2 \) production of the \( (\text{PAH} + \text{TiO}_2)_{7.0} (1:1) / \text{PAA}_{4.021} \) thin film.

4. CONCLUSIONS

This study demonstrated the efficient deposition of LbL films with subsequent adsorption of AuNPs. The TiO\(_2\) and HAuCl\(_4\) colloidal solutions showed absorption bands in the regions of wavelengths between 200 and 400 nm in the ultraviolet region (UV). By SEM and FTIR analysis, it was possible to verify the surface of BC and the main characteristic bands of cellulose, respectively. Moreover, it was proved by UV-Vis technique that AuNPs were incorporated in the thin films. Finally, by means of gas chromatography was possible to measure the \( H_2 \) production for the \( (\text{PAH} + \text{TiO}_2)_{7.0} (1:1) / \text{PAA}_{4.021} \) thin film which presented a photocatalytic potential of 1.96 \( \mu \text{mol cm}^{-2} \text{h}^{-1} \) of \( H_2 \).

5. ACKNOWLEDGEMENTS

The authors thank the Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPGERGS) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support.

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