Light-induced renewable hydrogen production through the photoreforming of a byproduct of the sugar alcohol industry

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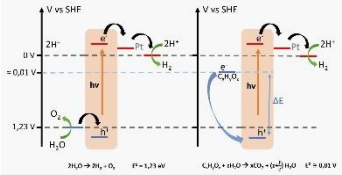

Solar energy conversion into clean fuels is an important research topic aiming at the energy transition. In this study, different semiconductors were evaluated as visible light photocatalysts (λ>400 nm) for the photoreforming of flegmass, a common and inexpensive residue from the sugar alcohol industry. The TiO_2-Pt photocatalyst was used as a benchmark to optimize the reaction conditions and in the following, ternary oxides and oxynitrides based on Nb(V) and Ti(IV) ions were evaluated as photocatalysts. The new material Nb/Ti oxynitride-Pt has yielded the highest H_2 evolution rate (545 µmol g^{-1}_{cat}) which is 10 times higher than that found for TiO_2-Pt. On the other hand, the use of the visible light absorbers $BiWO_6$ and $BiNbO_4$ did not yield to significant hydrogen evolution. The initial screening evidences the importance of the right photocatalyst selection for the photoreforming process, which is correlated to the band structure of the materials. Flegmass photoreforming can be an economically and environmentally promising alternative for hydrogen production from renewable sources.

Introduction

As the current most used energy source, fossil fuels are responsible for a large fraction of greenhouse gases, which pose a threat to the environment [1]. The use of alternative fuels has therefore been suggested in order to minimize emissions of polluting gases. H_2 production from renewable sources is a key energy vector towards fossil fuel replacement, however its production costs are still far above that from traditional natural gas reforming. Direct conversion of solar light into hydrogen by means of water splitting is potential solution although the current efficiencies are far below the point for upscaling. Alternatively, photoreforming of organic residues offers, kinetically and thermodynamically, a more favorable pathway for improving the H_2 production [2]. The selected substrate should be water soluble and largely available. Flegmass is residual water from the rectification of phlegm in distilleries, with traces of fusel oil and ethanol and very little added commercial value. Its use as a potential sacrificial agent in photocatalysis has not yet been explored. This study aims to reveal the potential of this industrial residue in the solar-induced photocatalytic hydrogen production.

Material and Methods

The flegmass effluent used was supplied by a sugar-alcohol industry located in the Minas Gerais triangle, Brazil. The titanium (Ti) and niobium (Nb) precursors were reduced to Ti and Nb nitride by calcination in an nitrogen (N_2) atmosphere using urea as the N_2 source and then the resulting material was calcined in an air atmosphere resulting in its partial oxidization and the formation of oxynitride. Bismuth tungstate and niobate (Bi_2WO_6 and $BiNbO_4$) were obtained by conventional hydrothermal synthesis, while the TiO_2-P25 used is commercial. The resulting material was then coated with Pt^0 (1% m/m) using the *in situ* platinum photoreduction method. The photocatalytic tests (>400 nm) in suspension were carried out in a borosilicate reactor in an inert atmosphere, sealed by a septum that allows the gases evolved during the experiment to be collected. Initially, the phlegmass concentration was evaluated using TiO_2-Pt as the reference photocatalyst, and the optimum concentration was used for the subsequent experiments. A Clarus 580 gas chromatograph (PerkinElmer) with a thermal conductivity detector (TCD) was used to monitor the evolution of H_2. The detector temperature was 250 °C and argon was used as the carrier gas.

Results and Discussion

The flegmass is a colorless liquid with an alcoholic odor, pH 4.75 and chemical oxygen demand (COD) of 409 mg L^{-1}. The concentration of flegmass strongly affects the photocatalytic evolution of H_2 as shown in Figure 1a using the benchmark TiO_2-Pt photocatalyst. The H_2 production dropped significantly with increasing dilution of the raw effluent: 42% and 83% drop after dilution to 50% (v/v) and 10% (v/v), respectively (Figure 1a). This trend indicates that the H2 evolution is dependent on the rate of the reaction between the photogenerated holes and the organic species in the substrate, which in turn seems to be dependent on the diffusion of the organic species to the TiO_2 surface. Based on this

result, the raw residue was employed without any further dilution in the photocatalytic tests with other semiconductors. In Figure 1b, it is shown the H_2 evolution as a function of the photocatalyst. For Bi_2WO_6-Pt and $BiNbO_4$-Pt, there was no significant H_2 evolution (H_2 evolution rate ≈ 0. 8 μmol g^{-1}cat h-1). This result is in line with the small observed decrease (3%) in COD for $BiNbO_4$-Pt, Figure 1c, which indicates that such photocatalysts are not able to effectively oxidize the organic species in flegmass under visible light illumination. The benchmark system, TiO_2-Pt exhibited a H_2 evolution rate of 6 μmol g^{-1}_{cat} h^{-1}, however, the new Nb/Ti oxynitride-Pt photocatalyst has shown the best performance with a production rate of 142 μmol g^{-1}_{cat} h^{-1}. The new Nb/Ti oxynitride material exhibits an anatase-like hexagonal structure as evidenced by DRX and Raman (Figure 2a,b), in which, N^{-3} and Nb(V) act as doping ions reduction the bandgap (Figure 3a) and improving the visible light harvesting in comparison with the pristine anatase TiO_2. XPS analysis confirm the N and Nb doping Figures 3b,c. Interesting, despite the high H_2 evolution rate observed for the flegmass photoreforming in the presence of Nb/Ti oxynitride, only a small decrease in the COD values, around 270 mg L^{-1} was observed after 5 hours irradiation (Figure 1c).

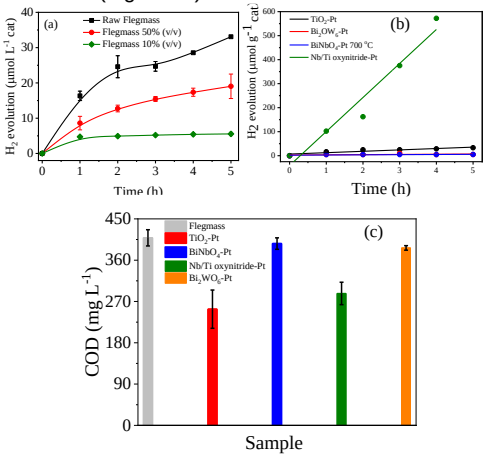

Figure 1. (a) effect of flegmasss dilution and (b) different photocatalysts on H_2 evolution and (c) COD removal.

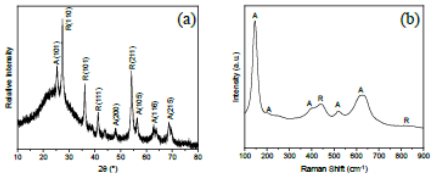

Figure 2. (a) X ray diffractogram and (b) Raman spectra of Nb/Ti oxynitride.

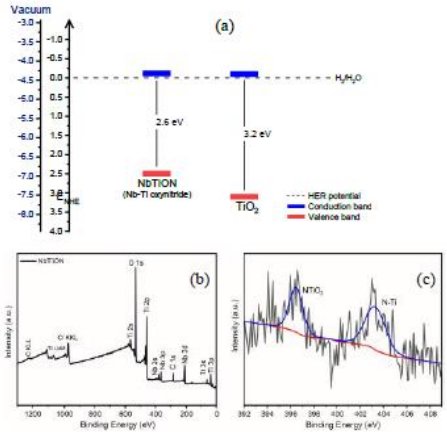

Figure 3. (a) Band edge levels of Nb/Ti oxynitride and TiO2 anatase; (b) Survey XPS spectra and (c) high resolution N1s spectra of Nb-Ti oxynitride.

Conclusions

Flegmass photoreforming is an interesting and poorly explored pathway for efficient photocatalytic H_2 production. In this work, the role of the flegmass concentration on the H_2 evolution rate was evaluated along with an initial screening of potential visible-light photocatalysts. Nb-Ti oxynitride-Pt was the most efficient photocatalyst among the investigated materials with a H_2 evolution rate of 500 μmol g^{-1}_{cat}. The new semiconductor exhibits improved visible light absorption and can lead to the selective oxidation of the C2-C4 alcohols avoiding mineralization and therefore being able to produce high-value chemicals concomitantly to the H_2 evolution.

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References

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