

Hydrogen generation by photocatalysis with BiVO_4

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 (Dated: June 11, 2022)

The aim of this work was to study the enhancement in photocatalytic hydrogen production by using BiVO_4 combined with Si solar cells.

I. THEORETICAL BACKGROUND

Photocatalysis is defined as the acceleration of a chemical reaction when a photocatalyst is exposed to light. Photocatalysts are semiconductors used as substrate that absorb light acting as a catalyst in the reaction. In this process, electron-hole pairs are generated, which at its turn generate free radicals that are able to undergo secondary reactions.

Recently, photocatalysis has been of great interest for hydrogen fuel production by photocatalytic water splitting (separating water into hydrogen and oxygen). The known environmental and health risks related to combustion of fossil fuels have made necessary the search of a greener alternative. Hydrolysis uses sunlight as its energy source and water as its main source for the reactants, both renewable and inexpensive resources. In addition, the product of the combustion of H_2 is water vapor. As such, photocatalysis is considered a green technology for converting solar energy into chemical energy without polluting the environment.

Titanium dioxide (TiO_2) is the most investigated and used compound. It is chemically stable, biologically benign and has the proper band structure to absorb UV radiation, oxidizing water to create hydroxyl radicals.

The main objective in the photocatalysis process is to avoid recombination of the carriers before reaching the surface to ensure the best results (similarly with what happens in energy production with solar cells). That means we want the charge carriers energetically and spatially separated.

For this, the main strategies consist on; (1) reducing the amount of sources of recombination in the volume and (2) in the external surface using, in each case, indirect band gap semiconductors to extend the lifetime of the charge carriers and by covering the external surface with a dielectric layer, and (3) incorporate selective contacts that specifically keep the carries physically separated.

There are two types of contacts or layers; Electron Transport Layers (ETLs), that allow the electron flow from where photocatalysis reactions take place and block the flow of holes to avoid recombination, and Hole Transport Layers (HTLs) that have the inverse effect, allowing the holes flow to react with the absorbed species while blocking electron transport.

TiO_2 is one of the dielectrics used for (2) in layers of around 1nm and its anatase form (tetragonal crystal structure) has shown good results in decreasing the internal recombination (1) and enhancing the performance of H_2 production.

Including selective contacts is key to avoid recombination in TiO_2 . For that we can either combine TiO_2 with a semiconductor with a different energy level, in our case BiVO_4 , or use a metallic catalyst on its surface such as Au or Pt. In both cases, we will create, in equilibrium, a zone of space charge, generating an energy barrier for the charge flow known as a Schottky barrier.

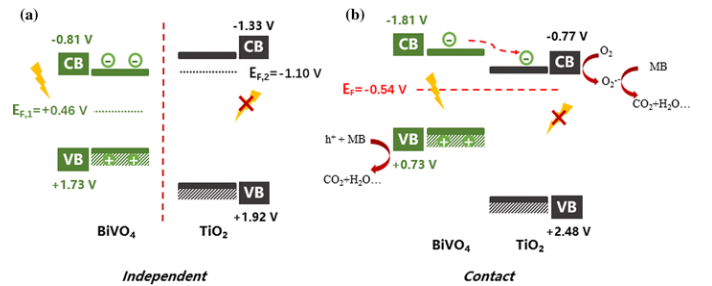


FIG. 1. Energy band diagram for a BiVO_4 and TiO_2 without any contact and b $\text{BiVO}_4/\text{TiO}_2$ heterostructures after thermodynamic equilibrium [1]

Pt is the most used co-catalyst for hydrogen production since it allows hydrogen production at low overpotentials by the formation of the Schottky barrier and its potential to entrap electrons. The efficiency of the Pt deposited on the surface of the photocatalyst (TiO_2) highly depends on its size, the loading, the interaction and the structure as well as the method used for its deposition on the photocatalyst surface.

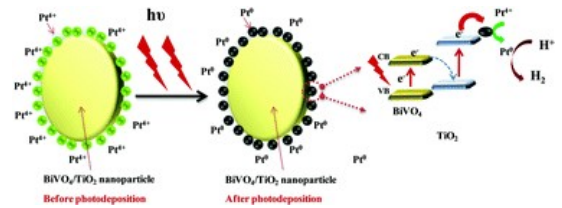


FIG. 2. Diagram of the $\text{BiVO}_4\text{-TiO}_2\text{-Pt}$ synthesis and structure. [2]

II. EXPERIMENTAL METHODS

Samples of $sg-TiO_2$, $sg-TiO_2-BiVO_4$ and $sg-TiO_2-BiVO_4/Pt$ were needed and synthesised in the laboratory. The samples are placed on a silicon wafer, covered with a dielectric layer (like SiO_2 or Al_2O_3) on top, and then cut into squares of $2cm \times 2cm$.

Silicon wafers were chosen because their flatness, versatility, availability and cheap price compared to other supports that could withstand the fabrication process (like quartz). In addition, silicon is inert to the reaction.

A. TiO_2 sol-gel synthesis

Sol-gel process is a method for producing solid materials from small molecules [3], and is used in the fabrication of metal oxides, in our case titanium oxides, that will be used as the photocatalyst.

For this purpose we used titanium propoxide, distilled water, ethanol and hydrochloric acid. To avoid the hydrolysis of the titanium isopropoxide with air humidity we need to create an inert atmosphere [4].

First an Ar atmosphere is created in an oven dried beaker with a cylindrical piece, that will later be used to mix the compounds. Afterwards we add 5g of titanium isopropoxide, changing the pipette when needed to avoid hydroxylation at the pipette's tip. Then, we add 5g of ethanol. Once added, we quickly change the beaker from the scale to a magnetic stirrer with a N_2 atmosphere. While stirring, we add 1mL of hydrochloric acid and then 2mL of water, drop by drop. After that, we leave the mixture for 10-15 min stirring, and then we add 100mL of ethanol and leave it stirring for another 10 more min.

If, during the process, we detect any sign of hydrolyzation, that is, crystallization, solidification of the mixture or appearance of a white top coat, the mixture is not valid and the process must be repeated. The obtained sol solution is then stored in a fridge and can be used 15 days from the date of preparation.

The obtained sol is a gel-like system containing both a liquid and a solid phase, and in order to recognize the gel-like properties, a great amount of liquid, or solvent, must be removed. To do so, we require a drying process. For that, we deposit thin films of TiO_2 on a pre-cut Si substrate, ensuring a good coverage of all the area. Then it is left drying during 24h to be lastly calcined for 4h at $500^\circ C$. To obtain a film as uniform as possible, temperature is increased/ decreased $5^\circ C/min$.

The resulted films weigh 2-3g and are 1mm thick.



FIG. 3. Sol-gel synthesis process

B. $BiVO_4$ powder synthesis

The bismuth vanadate powder used for this work was synthesized following the method explained in [5]. A mix of two solutions is made to obtain the precursor substance with precipitated Bi_2O_3 . We then placed the solution into a furnace at 500° , until a yellow foamy and voluminous powder is produced as the product of combustion after 20 minutes approximately. For every 2.0-2.5ml of precursor solution, 200-250mg of SVC- $BiVO_4$ was obtained.

C. Photo-deposition of Pt

Photo-deposition was used to deposit metallic nanoparticles on the different photocatalyst nanopowders, maintaining a 1:100 ratio between the metal and the semiconductor.

To begin with, a solution of 25ml of distilled water and the precursor corresponding to 1mg of metal is stirred for 10 minutes. Then, 100mg of the photocatalyst are added before stirring for 10 more minutes. Finally, 25ml of ethanol are added and the solution is left stirring for 12 hours under UV light.

After the 12 hours, the solution is centrifuged at 10krpm for 25 minutes in order to precipitate the resulting nanoparticles to the bottom of the recipient. The solid is transferred to another ceramic recipient to be dried at $70^\circ C$ during 12 more hours.

D. Metal nanoparticles by drop-casting

For our silicon supported samples, photodeposition is not an option [6]. For that reason, the Pt in the samples is deposited by drop casting.

To deposit the platinum over the sol-gel TiO_2 samples, we drop a quantity of precursor corresponding to the

100:1 ratio between TiO_2 and Pt. It is a procedure done over a flat surface and over several steps, where the sample is covered with precursor and then dried at 70°C to avoid spilling it out of the surface.

After all the precursor is casted and dried, the sample undergoes a heat treatment at 300°C for an hour in order to form the metallic nanoparticles.

E. Reactor set-up and hydrogen production tests

The system consists of a glass reactor, sealed with parafilm in order to avoid gas leaks, that is connected to an illuminator lamp that emits light at our desired bandwidth (from visible to UV). The reactor is also connected to the bubbler (4)), the test tube where the reactants will be moved by the Ar gas flow, using stainless steel cables and connections that must be thoroughly fixed and sealed so that we minimize gas leaking.

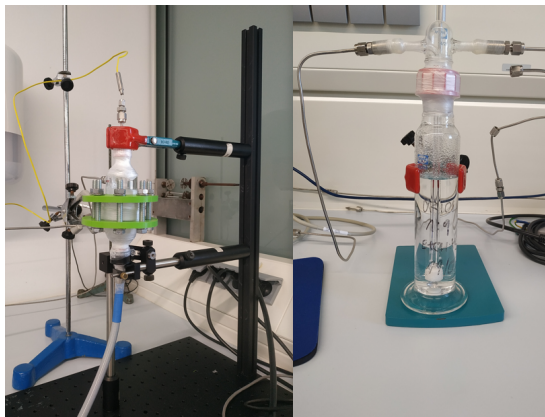


FIG. 4. Left: Bubbler with the reactants. Right: Reactor system

Inside the reactor, we find the plastic support where our samples will be placed for measurements, as well as a thermocouple that measures the temperature inside the glass capsule.

Lastly, the outlet of the reactor, which corresponds to the gas products of the reaction, is connected through another cable to the GC (or a Gas Chromatography device) for making the measurements and comparing the concentration of products, in other words, the production of hydrogen of the different samples.

Our measurements will consist of placing a sample on the reactor, and measuring the concentration of H_2 produced as a function of time. Then, following the same procedure for different samples, we will compare the results and arrive at a conclusion.

III. RESULTS AND DISCUSSION

The obtained production rates are normalized by the total mass of the nanoparticles used. Given that we want to compare it for the different samples, we apply the following conversion factor:

$$\frac{20\text{mL}}{\text{min}} \cdot \frac{X_{H_2}\text{ml}}{100\text{ml}} \cdot \frac{1\text{L}}{1000\text{ml}} \cdot \frac{1\text{mol}H_2}{24.4\text{L}} \cdot \frac{10^6\mu\text{mol}}{1\text{mol}} \longrightarrow [\mu\text{mol}/\text{min}]$$

where $X_{H_2}\text{ml}$ is expressed as a percentage and the conversion factor from mol of H_2 to L has been obtained by applying the ideal gas law for a temperature of 298°K . We will also divide this production rate by the mass of photocatalyst used, so that the rates can be normalized and properly compared.

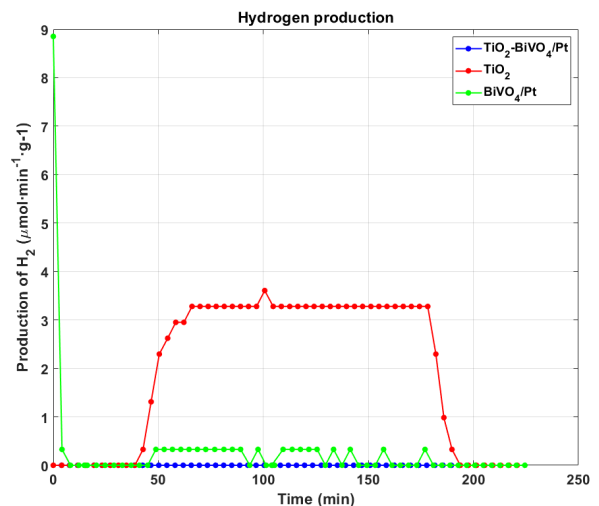


FIG. 5. Hydrogen production rate against the reaction time.

Looking at (5), the first thing that we can notice is that the production of our composite $TiO_2 - BiVO_4/Pt$ is much less than expected, in fact, it produces less hydrogen than the minimum resolution of the GC. This may be because the properties of the Pt co-catalysts on the $BiVO_4/TiO_2$ composites strongly depend on the dispersion and anchoring contact between them, so it could be that our sample did not have these connected properly, producing much less hydrogen than expected. Next, we can tell that the production of acetaldehyde is greater than that of H_2 , and that can be explained by taking into account that hydrogen can recombine with the remaining oxygen inside the reactor that has not yet been purged. Therefore, if we made the same reaction in a proper vacuum, we would expect to measure more H_2 produced.

Another comparison that we can make is between our sample of $BiVO_4/Pt$ with the same one in [6], and conclude that our composite of this particular nanoparticle yields more product. The reason for that could be that

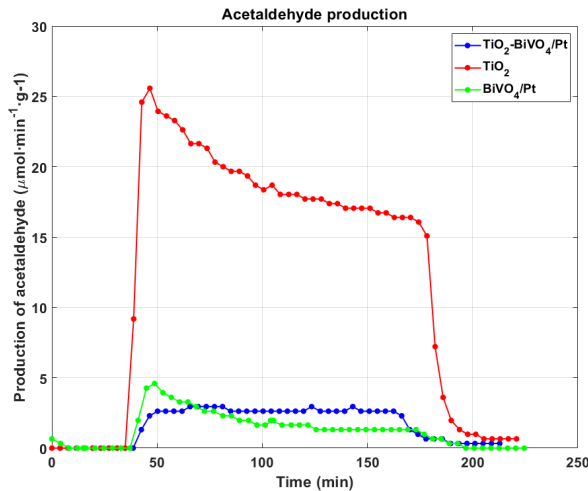


FIG. 6. Acetaldehyde production rate against the reaction time.

the settings of our illuminator were different than the ones used for said measurement. As more radiation is reaching our sample, an increase in the generation of hydrogen can be expected.

IV. CONCLUSIONS

The results that we obtained are not exactly what we initially expected. While the TiO_2 sample yielded similar results as in [6], we believed that adding $BiVO_4$ to our sample would increase the production of hydrogen. On the one hand, we can affirm that TiO_2 works properly as a photocatalyst for the hydrogen production reaction from ethanol.

Contrary to what we initially expected, the addition of

Pt did not improve the results, and additional samples should be tested to determine whether its due to the experimental method used to make the sample or not.

Further experiments are being done to improve hydrogen production. Latest samples with gold acting as an HTL and magnesium as an ETL show very promising results, opening new possibilities in the research of higher quality samples for hydrogen production.

V. REFERENCES

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