



Study of CdS doped with Cu for hydrogen production through Photocatalysis.

Estudio de catalizador de CdS enriquecido con Cu para
producción de hidrógeno mediante fotocátalisis

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1. Abstract

Este estudio se centra en la utilización de catalizadores de CdS para producir hidrógeno debido a su interés como fuente de energía.

La importancia de las energías renovables y limpias ha ido creciendo en los últimos años. En este sentido tenemos la energía que nos llega del sol en forma de radiación, iluminando, provocando los vientos, calentando el aire y las aguas y dando lugar a la alimentación autótrofa de las plantas a través de la fotosíntesis. Con la energía solar una planta puede superar los niveles de energía necesarios para iniciar reacciones químicas que les permite continuar su desarrollo y sobrevivir. La utilización de la energía solar para iniciar una reacción parecida se puede utilizar para producir hidrógeno mediante la hidrólisis del agua, popularizada como proceso de “Water-Splitting”, separación de agua.

Existen diversos estudios en la materia, que comprenden desde las bases teóricas del proceso y la energía necesaria para iniciar la reacción, su eficiencia, catalizadores para mejorarla y los denominados “agentes de sacrificio”. Los agentes de sacrificio son reactivos utilizados para mejorar la reacción que se consumen en el proceso, pero de los que a priori no se obtiene hidrógeno.

Este hidrógeno una vez obtenido puede ser utilizado como combustible. La combustión del hidrógeno tiene la ventaja de que deja como único residuo agua, el cual, aunque es un gas de efecto invernadero, puede entrar en el ciclo natural del agua. De esta forma se obtendría una fuente de energía renovable y limpia.

Al proceso se le denomina de una forma más técnica como fotocátalisis, foto por luz y catálisis porque produce la ruptura de las moléculas. En un ambiente controlado de laboratorio, el agua para obtener hidrógeno y los agentes reactivos para dar lugar a la reacción se introducen juntos en un reactor dentro de un sistema cerrado y controlado, sometidos a una luz de unas lámparas conocidas con el dispositivo conectado a un espectrómetro de masas que controla el hidrógeno obtenido.

En estos experimentos lo que se ha estudiado en concreto es la eficiencia del catalizador, manteniendo el resto de los parámetros fijos. Para ello se han realizado tanto la síntesis del compuesto, CdS en este caso, como del procesado de este y la prueba de fotocátalisis en un entorno controlado.

Para las síntesis se han utilizado dos métodos: uno consistente en la mezcla de reactivos que se calienta en un horno hidrotermal asistido por microondas y otro en un método de reflujo en que se mezclan los compuestos y se someten a temperaturas cercanas a la ebullición del agua en condiciones estándar. En el primero se utiliza como medio etilendiamina, y se trata $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ con tiourea en una proporción molar de Cd:S como 1:1. Para el segundo se utiliza una solución de 10% H_2O , 30% 1-butanol and 60%

etilendiamina en las que se combinan $\text{Cd}(\text{CO}_2)_3$ y CS_2 . Ambos procesos toman tiempos similares, pero el primero es más simple y requiere menos vigilancia del operador.

Los productos obtenidos por el primer método se estudiaron por difracción de rayos X. Los patrones de difracción obtenidos coinciden con los de otras investigaciones con lo que se confirma que el compuesto obtenido es efectivamente CdS. La identificación por difracción de rayos x para los productos obtenidos por el otro método aún están a la espera, por problemas en el SEGAI.

Los compuestos de CdS fueron posteriormente dopados con Cu. En anteriores investigaciones se muestra que la adhesión de metales puede incrementar la eficiencia del reactivo. Los difractogramas de rayos X se hicieron para los compuestos del primer método, las otras están en espera para pruebas. También coinciden los patrones. Se hizo una prueba de microscopía electrónica para el compuesto dopado al 1% observándose un hábitat de barras hexagonales de unos 50-100 micrómetros.

El dispositivo utilizado para la fotocatalisis está compuesto por una caja en cuyo interior se encuentran un soporte del reactor con agitación magnética, dos lámparas, una de luz visible y otra de UV, una cobertura metálica con forma elíptica que aprovecha las propiedades de los focos para dirigir uniformemente los rayos a la zona del reactor. Encima del soporte se coloca el reactor, el cuál dispone de una camisa externa para mantenerlo a temperatura controlada, con los reactivos en su interior. Se conecta a un gas de purga, nitrógeno, y a un espectrómetro de masas que se encarga de tomar las medidas cuantitativas de hidrógeno. Después de la purga se somete la muestra habitualmente a 100 min de luz visible y otros 100 de luz ultravioleta. Luego se separa y se guarda.

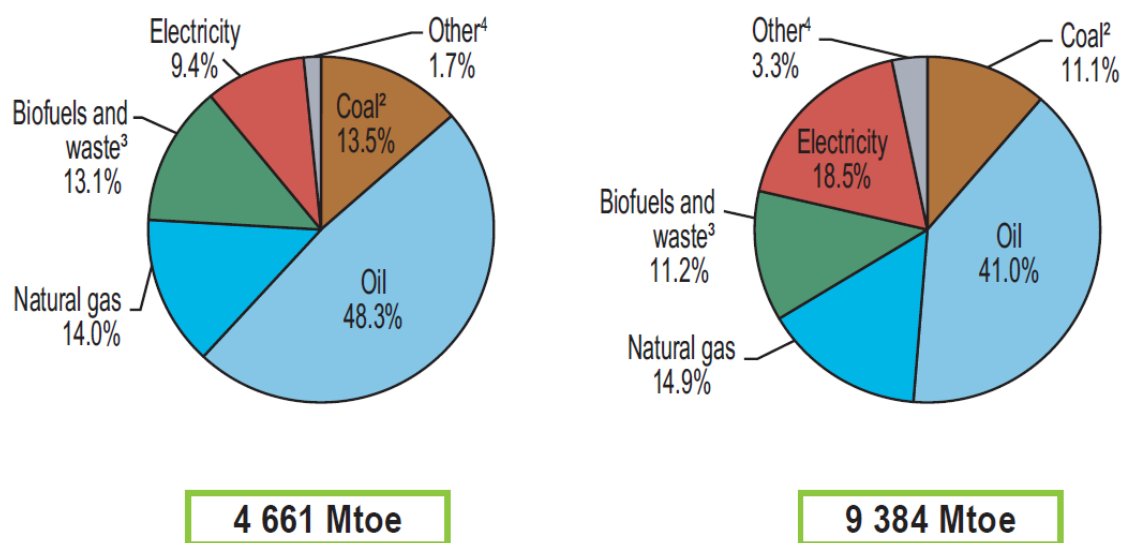
En otras investigaciones previas, se ha observado que la adición de metales incrementa la eficiencia. Esto parece ser así sólo para algunos casos, pareciendo obtenerse una mayor eficiencia general para el dopado en masa al 1% de Cu en CdS. Se exceptúa en el rango de UV para uno de los compuestos del método de síntesis con el horno hidrotermal. Sin embargo, en comparación con más experimentos del mismo laboratorio este resultado resulta atípico y necesita repetirse para confirmarlo, ya que da mayor eficiencia que el resto de los compuestos. Exceptuando ese caso parece que el método de reflujo tiene una eficiencia mayor.

Los resultados obtenidos en este estudio parecen remarcar la importancia de la estructura cristalina como principal factor influyente en la eficiencia. Sería recomendable realizar más pruebas para conocer mejor la estructura de los que aún no han podido ser estudiados y determinar un método óptimo para conseguir un sistema más efectivo.

2. Introduction

En este capítulo se trata la importancia del hidrógeno, tanto su utilidad social como comercial y posibles usos; las bases teóricas implicadas en el proceso de fotocatalisis e investigaciones previas que han sido útiles y necesarias para la realización de este proyecto.

World energy consumption has generally and greatly increased since the industrial era. Most of the energy supplies consumed comes from no-renewable energy sources, as seen in figure 1.



1. World includes international aviation and international marine bunkers.
2. In these graphs, peat and oil shale are aggregated with coal.
3. Data for biofuels and waste final consumption have been estimated for a number of countries.
4. Includes heat, solar thermal and geothermal.

Figure 1. Data of fuel consumption in 1973 (left) and 2015 (right) [1]

Specifically, the energy for 2015 is approximately 109135920 GWH [2]. Most of the shown sources that appeared to power that consumption in figure 1 are from non-renewable fuels. Once depleted, there will be a need for new sources, as for example, incoming solar radiation. According to Nasa measurements the energy reaching top of the atmosphere is 1.36 kw per square metre (directly facing the sun) [3].

Solar radiation is an important incoming energy source to Earth, powering weather through all of it, visible light for our daily life and direct radiation which has been used to power solar cells and keeps increasing. It had also been powering life for millions of

years since its heat allows chemical reactions necessary for life. There are also some living beings which have taken a great advantage of this: photosynthetic living organisms.

As it is commonly known, photosynthesis is the process which plants take energy from the sun to turn it into food. That is a typical definition we can find in dictionaries, such as Cambridge's dictionary or in a quick look through the web. More interesting ones are these:

“Synthesis of chemical compounds with the aid of radiant energy and especially light” [4]

“Formation of carbohydrates from carbon dioxide and a source of hydrogen (as water) in the chlorophyll-containing cells (as of green plants) exposed to light” [4]

Artificial photosynthesis is inspired by the concept of the feeding process done by plants, takes a more similar approach to this definition to follow the research based on it. The main aim of these researches is to find a process to obtain an environmentally friendly and renewable source for energy, not just for energy production but also to solve problem like storage since the consist as seen in the first definition above that they are synthesized in chemical compounds, such as hydrogen.

Water-Splitting is a simple method of catalysis, with some resemblance to photosynthesis, using light as energy to drive the reaction [5]. Moreover, it is not just a renewable source but also a clean one. Climate change is an important issue nowadays (figure 2) that affect Earth and prospective future for any human related activity. The increasing in temperature mainly increases water level of the oceans, reducing available land to sustain terrestrial life.

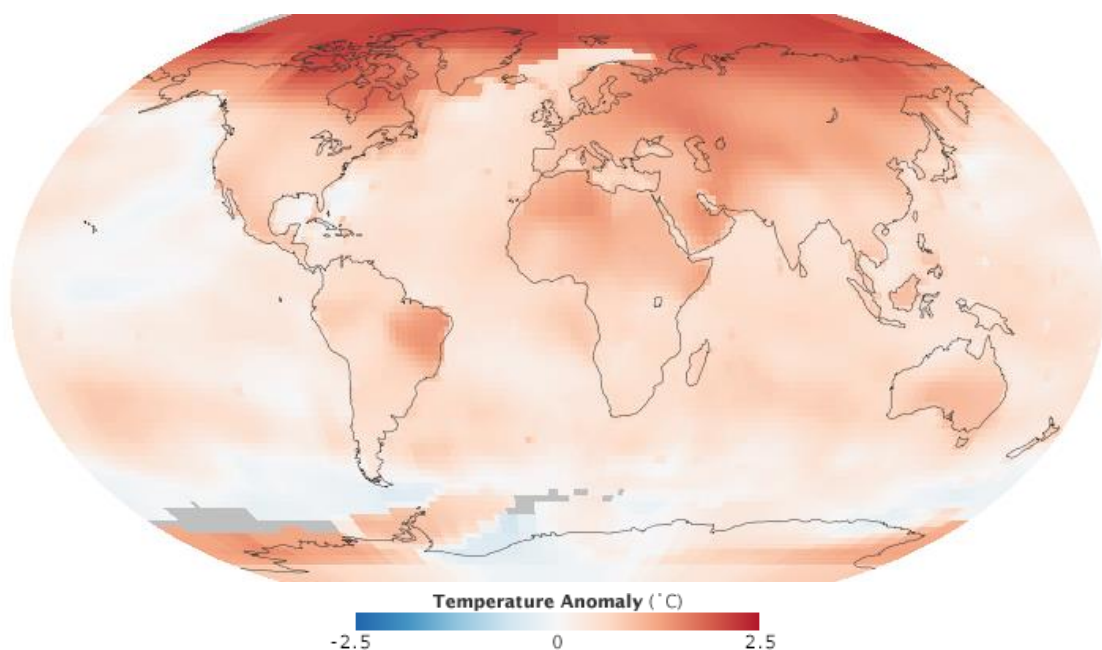
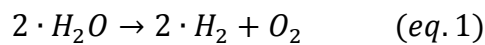


Figure 2. Average temperature change from 2004-14. [6]

In addition, energy production is a main factor to deal with climate change due to greenhouse gases contribution. Since Water-Splitting does not produce greenhouse gases (water is included under natural water-cycle and its problems are mainly related to temperature changes) and it is supposed to be powered through incoming solar radiation, it can be used to deal with climate change and energy crisis.

2.1 Photocatalytic Water Splitting

One of the main process of artificial photosynthesis is photocatalytic water splitting to obtain H₂ through photoelectrolysis. The reaction to take place would be:



With a more schematic representation:

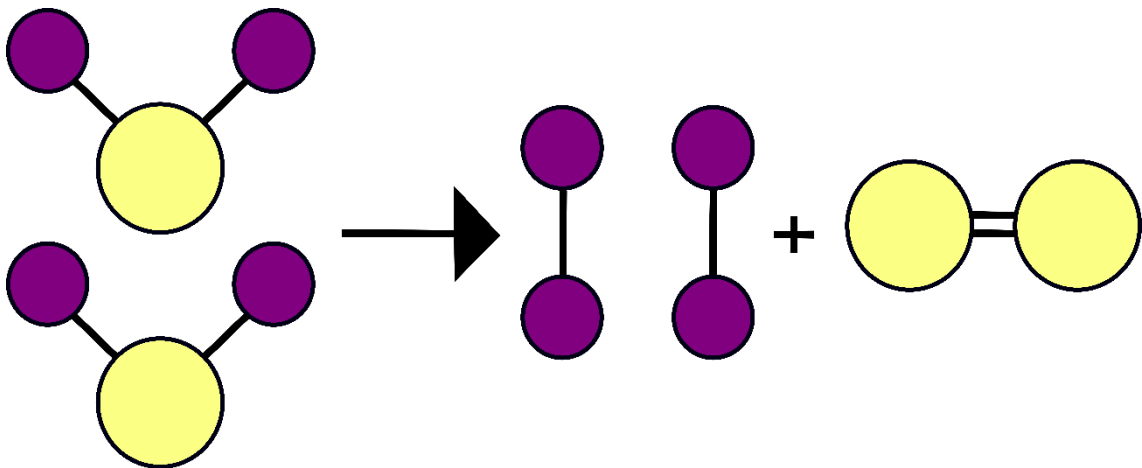
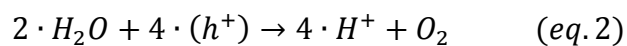


Figure 3. Water combustion. Hydrogen atoms in purple, oxygen atoms in pale yellow.

This reaction takes place through a reduction and an oxidation. To carry these processes, we account that hydrogen atoms have valence +1 and oxygen ones have valence +2. [4, 7]

The reduction:



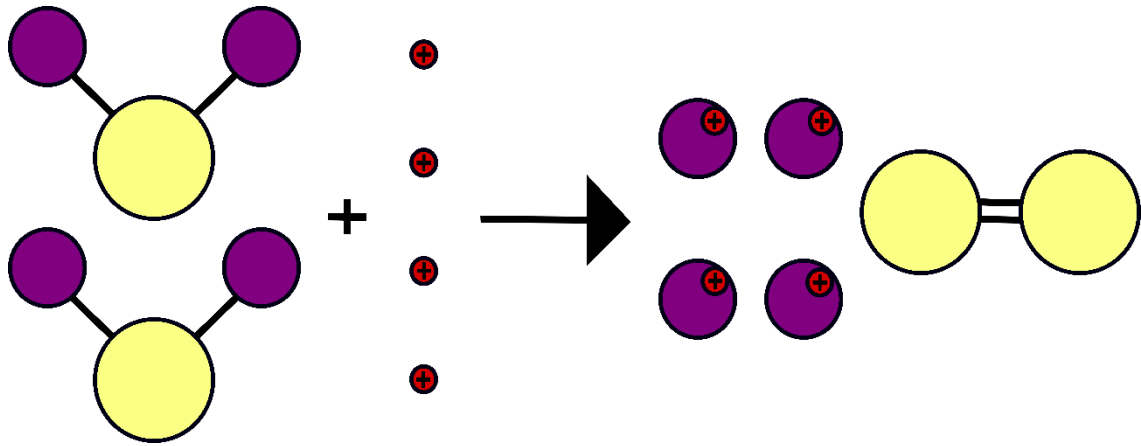


Figure 4. Water oxidation.

Then the oxidation for hydrogen takes place:

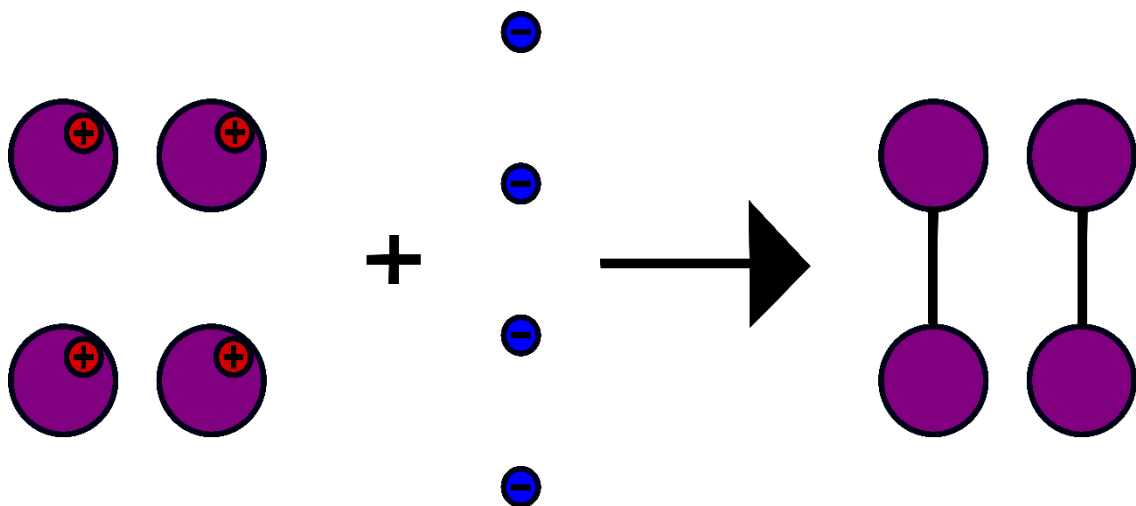
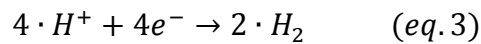


Figure 5. Hydrogen reduction.

That information is enough to calculate the Gibbs energy, which is the energy necessary to drive the reaction.

According to thermodynamics laws [8] the enthalpy can be calculated with the known values of each molecule bond matching figure 3. For the water molecule we have two bonds H-O, with energy 460 kJ/mol each one; for hydrogen molecule we have H-H with 435.88 kJ/mol and an oxygen molecule O=O with 493.4 kJ/mol [9]. So, the equation will be:

$$\begin{aligned} \text{Potencial energy product bonds} - \text{Potencial energy reagents bonds} &= \text{reaction energy} \\ (2 \cdot 435.88 + 493.4) - 4 \cdot 460 &= -474.84 \text{ kJ/mol} \quad (eq.4) \end{aligned}$$

Dividing into the oxidation (figure 4) and the reduction (figure 5) there is for the first one:

$$493.4 - 4 \cdot 460 = -1\,346.6 \text{ kJ/mol} \quad (\text{eq. 5})$$

Since this potential must be measured in the reduction direction the value is:

$$1\,346.6 \text{ kJ/mol}$$

And for the second one:

$$2 \cdot 435.88 = 871.76 \text{ kJ/mol} \quad (\text{eq. 6})$$

Now it is possible to use the Nernst equation [10, 11] calculate the potential of the hypothetical galvanic cell:

$$E^o = -\frac{\Delta G_R^o}{nF} \quad (\text{eq. 7})$$

Where ΔG_R^o is the change in the free Gibbs energy, n is the number of mol and the Faraday constant with value 96 485 C.

So the gap for the reduction process per two mol of H₂ (four electron involved) is (figure 5):

$$E_{red}^o = -\frac{871\,760}{4 \cdot 96\,485} = -2.2587967 \text{ V}$$

The gap for the oxidation process per two mol of H₂O is (figure 5):

$$E_{oxd}^o = -\frac{1\,346\,600}{4 \cdot 96\,485} = -3.4891434 \text{ V}$$

The difference:

$$\Delta E^o = E_{red}^o - E_{oxd}^o = -2.2587967 + 3.4891434 = 1.2303467 \text{ V} \approx 1.23 \text{ V}$$

That difference, 1.23 V, would be the gap energy for an electron to be released. As seen for this reaction (figure 1, 2 and 3 and reaction 1, 2 and 3), for two mol of water there are four electrons to be freed. This will make the energy gap to be $4 \cdot 1.23 \text{ V} = 4.92 \text{ V}$.

This reaction can be drive using a semiconductor as a catalyst which must be able to absorb radiant light with photon energies larger than 1.23V. In the ideal case, a single semiconductor material having a band gap energy (E_g) large enough to split water (greater than 1.23eV) and having a conduction band-edge energy and valence band-edge energy that straddles the electrochemical potentials for the products will be enough to drive the reaction. The electrons and holes generated in the semiconductor as a result of this process must travel to a liquid junction and must react only with solution species directly at the semiconductor surface to avoid recombination. This produces losses due to the concentration and kinetic overpotentials needed to drive the evolutions of H₂ and O₂, so the practical need reported due to these losses is between 1.6 and 2.4 eV. [4]

2.2 Former research.

In this research catalysts to enhance hydrogen production (through photocatalysis) have been studied. There is previous research about this issue that concentrated in a specific catalyst, CdS (Cadmium Sulfide) doped with Cu, Ni and Au. [13] The method shown in that paper (synthesis shown in 4.2.2, and photodeposition) have been reproduce as a reference to compare to the result of other variables of the research since the experimental device for the photocatalysis is different.

In our lab the doping with Cu and Ni have been tried, and specifically this paper shows results related with CdS and CdS doped with Cu. Prior to this study, in our lab other doping methods have been studied and different sacrificial reagents, giving specific parameters for concentration of them and the catalyst. [14]

In those previous studies done in our lab, CdS synthesis method was through a hydrothermal oven assisted with microwaves, explained in section 4.2.1. The doping method was through ultrasounds and in this paper, it is shown photodeposition method, same as in the paper reference in the first paragraph of this section. Also, calcination was added to some of the compounds.

One of the compounds appeared to be especially efficient compared to the other compounds. After XRD results it was shown that it was contaminated with CdCO_3 (extended in section 4.2.3), so it a mix of them was synthetized for trial.

In general, due to the previous research, mass concentration of Cu for doping were chosen to be around 1%, which is the value that showed larger production.

3. Objectives

En este apartado se exponen las expectativas sobre el proyecto y la finalidad última de investigaciones de esta clase.

The objectives are to produce Hydrogen as a clean and renewable source of energy to be later used for society benefits. There are two huge points that affect its spreading as a common energy source: production and storage. This would be an early stage of the process necessary to make getting hydrogen as profitable as other renewable sources or efficient enough to surpass the costs of producing. Renewable sources are usually tied to the environment, such as solar and wind energy, which work well to get electrical energy.

Advantages of hydrogen are its high energy production through combustion per mass unit, though not so good per volume. Also, the combustion residue is only water and the combustion engine is a widely known technology which most transports are adapted to. That could allow to make massive vehicles (as well as planes) clean and with no need for charging (for electrical ones) since hydrogen will be used just like any fuel [15].

The photocatalytic reaction is thought to be powered by solar energy when there is an excess, for example.

To achieve this, we have studied different particle morphologies for the CdS, doping methods and Cu mass concentration rate to CdS and subjected to diverse radiation tests, exposing it to visible and UV light.

Then hydrogen production is measured using a mass spectrometer connected in-line with the reactor output and controlled by a computer.



Figure 6. Photocatalyst device.

For characterization of particles TEM and XRD test have been taken. These parts will be extended below.

4. Experimental Process

En este capítulo se explican todos los procesos seguidos durante la investigación y se especifica los materiales implicados.

The whole process can be divided into three parts, with each one need special attention and characterization: synthesis, doping and radiation test.

4.1 Experimental material

4.1.1 Photocatalysis device

The main component of the device is a wooden cage inside which the photocatalysis process will take place. There is a magnetic stirrer below the apparatus. There are two lamps, one of visible light and the other one of UV. There are tubes which connect with the reactor, the purge gas and the spectrometer. The one with the mass spectrometer has a draining system attached to avoid humidity affecting the spectrometer. There is a deformed cylindrical metal platen surrounding vertically the whole photocatalytic device. This design enhances light projection.



Figure 7 a. (left) Photocatalyst cage, with lamp controllers and the draining system. 10 b (right) Inside the cage

The metal platen is shaped as an ellipsis to take advantages of the focal properties of them. If you trace a line from one focal point to the cover, following the reflection law, which states that the angles for the incident and the reflected ray are the same, the line will reach the other focal point.

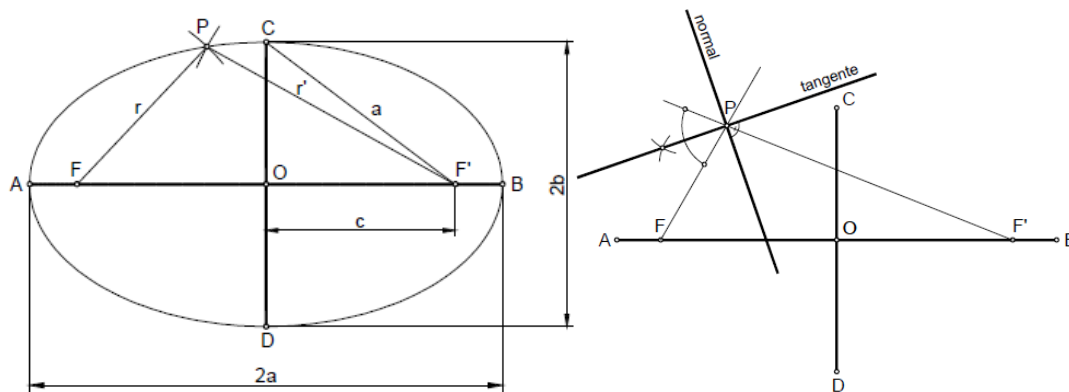


Figure 8. Ellipse on the left, detailed tangent on the right. [16]

The lamps are placed in the focuses F and all the lights reflected on focus F' achieving the maximum radiation on the reactor (focus F').

There is also a system to stabilize temperature, using an external thermostat with a continuous waterflow in the external jacket of the reactor.



Figure 9 a (left) Spectrometer. 10 b (center) Thermal control. 10 c (right) Purge gas Manometer



Figure 10 a (left) Detailed of lamp control. 12 b (right) Lamps inside the cage, with a fan for cooling.

Models:

1. Lamps:

1.1 Visible: Lauci Classic Linear Halogen, 500W

1.2 UV: Philips HDA Synergy, 300W

2. Spectrometer: Pfeiffer Vacuum OmniStar™

4.1.2 Hydrothermal furnace assisted by microwave

This device, which have been used for several synthesis, consists of a hydrothermal system with pressure and temperature control. It uses microwaves to heat. Once the process is over it is let to cool down at room temperature.



Figure 11. Reactor for the furnace, useful for 60ml of solution. The stick is for temperature control.

The program shows continuously the pressure and the curve of heating, it also allows to choose temperature ramp rate and dwell time. It is easy and fast to use, and it can be let to work alone. A typical experiment last 0.5-2h.



Figure 12 a. (left) Reactor inside the furnace. (center) Pump device.

Model:

Milestone Ethos Plus-1 Microwave Digestion Hydrolysis Evaporation Sample Prep.

4.1.3 Calcination furnace

For the calcination of compounds, a convection furnace was used, equipped with a digital controller to control heating dwell, temperature and thermal ramps. A typical calcination consisted on heating at a rate of 5° per minute up to 350° and a dwell of 8 hours at that temperature, then cooled at a similar ramp up to 90° and then alone up to room temperature.



Figure 13 a (left) Oven. 15 b. (right) Controller.

Model:

Hornos eléctricos Gallur 606, till 1300°C

4.1.4 Centrifugation device

To separate the solids from the different solutions a centrifugation device was used. It has special containers of two different sizes. These containers were also used for washing the products.



Figure 14 a. (left) Inside of the centrifugation device. 16 b. (right) Containers for centrifugation.

Model:

Kendro, Heraeus Megafuge 1.0R

4.1.5 Reflux synthesis material

For this process, there have been used the following materials:

1. Reflux system
2. Heating plate
3. Thermometer
4. Round flask
5. Magnet for stirring
6. Support
7. Oil
8. Glass container for oil.
9. High Vacuum grease

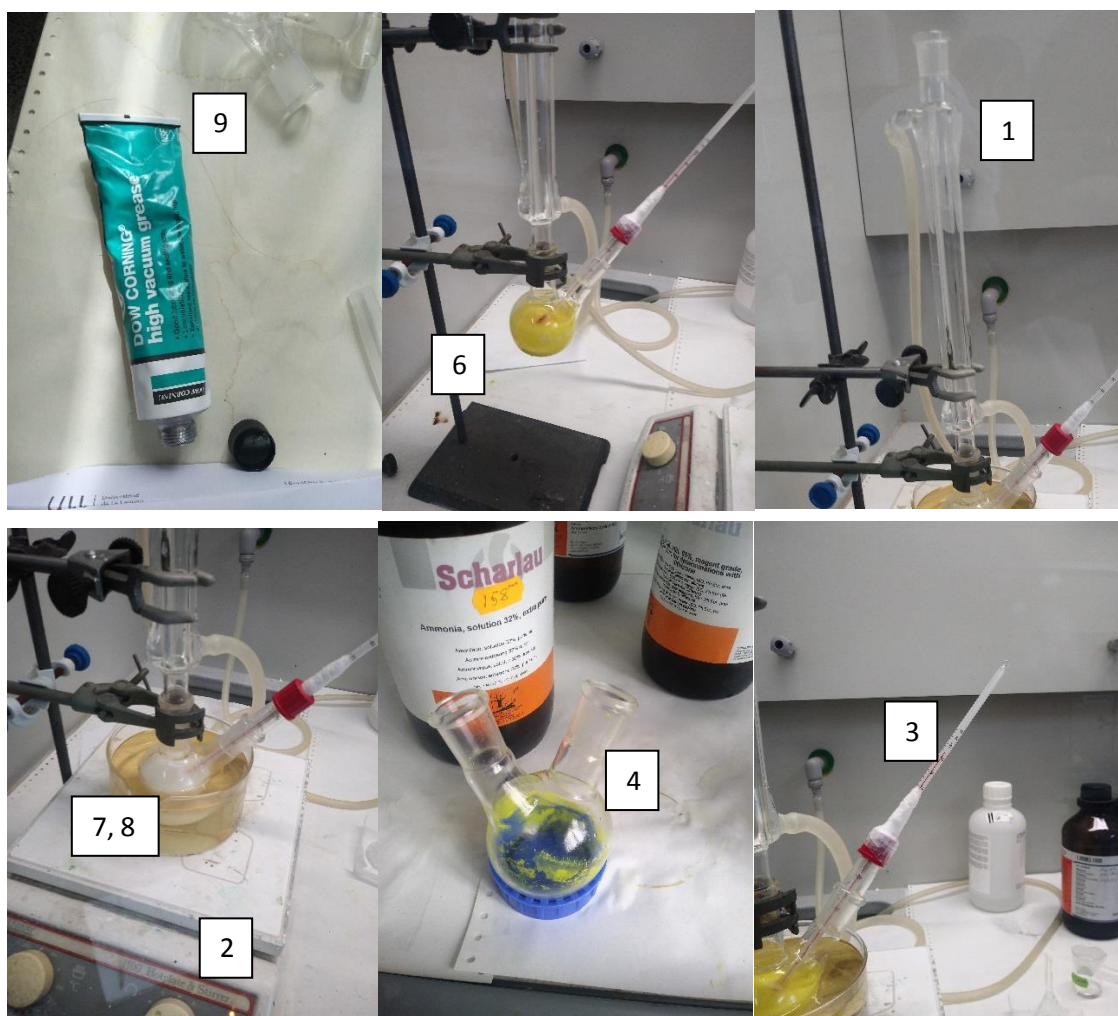


Figure 15. Different devices, each one labelled according to the numbers in the list.

4.1.6 Heaters

Two different ovens were used for drying the compounds after washing due to technical needs of researchers in the lab. They were used from 60° to 80°.

Models:

Figure 16a: Heraeus Thermo Scientific

Figure 16b:



Figure 16a on the left, b on the right. Ovens

4.2 Synthesis

4.2.1 CdS synthesis through a hydrothermal furnace assisted by microwave

The whole process consists of the reaction of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ with thiourea in an ethylenediamine solution.

1. Reagents were weighted using an analytical balance, in a molar proportion of 1:1, so 4.62g of both $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and thiourea mass were used.
2. The reagents were mixed with 60mL of ethylenediamine in the oven reactor
3. Then the reactor was taken into the furnace at 150°C during 2h.



Figure 17 a. Reactor scheme. 2b Reactor Photo

4. After the reactor was cooled to room temperature it is centrifuged and then washed at least two times with water and two times with ethanol.
5. Finally, products were grinded and preserved in appropriate containers.

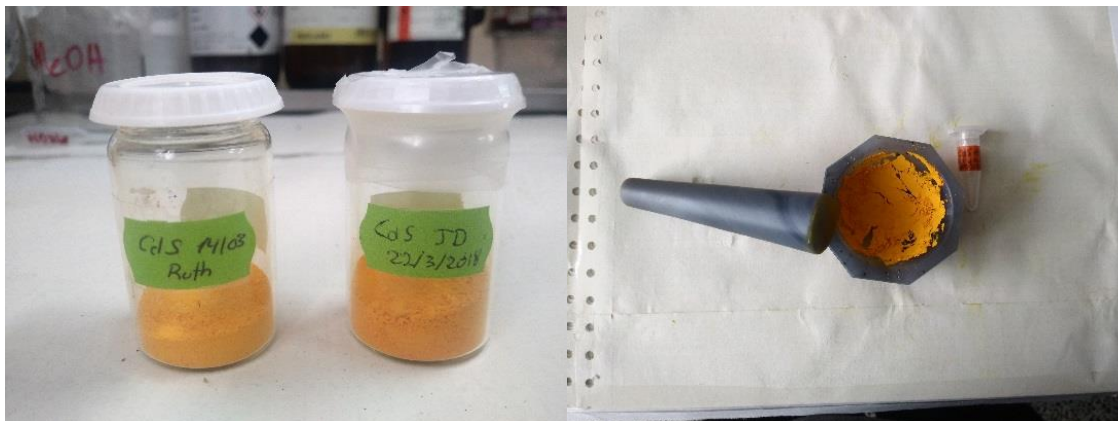


Figure 18a (left). Example of containers. Figure 3b (right). Example of grinding and other type of container.

Samples of these powders were analyzed by XRD and CdS/Cu 1% was also analyzed by TEM.

4.2.2 Synthesis through reflux

This is an alternate to the synthesis to the first one tried. It is referred in a prior paper by Oros Ruiz et al [13]. This has been made to check that we were able to reproduce their results and to compare them to our own results. The synthesis is made with $\text{Cd}(\text{NO}_3)_2$ and CS_2 in a solution of 10% H_2O , 30% 1-butanol and 60% ethylenediamine. The process consists of:

1. 6ml of H_2O and 18mL of 1-butanol are measured and poured into a round flask connected to a thermometer. Then it was stirred.
2. 4.2702 g of $\text{Cd}(\text{NO}_3)_2$ were weighed and spilled into the round flask.
3. Constant stirring during 15 mins at room temperature, or up to a complete mixed is achieved.
4. 36mL of ethylenediamine were measured and poured into the flask.
5. 0.5270 g of CS_2 were added into the round flask.
6. The water refrigerator was then connected to the flask and the mixed is heated to a temperature between 90°C and 110°C .
7. Once the desired temperature was reached it was kept at this temperature.



Figure 19. Full device

8. After this process was finished the round flask with the mix is cooled to room temperature, centrifugated, washed once with H₂O and once with EtOH, dried and finally grinded and kept in a suitable container.

As shown in the figures, the color changed during the process from white to yellow.

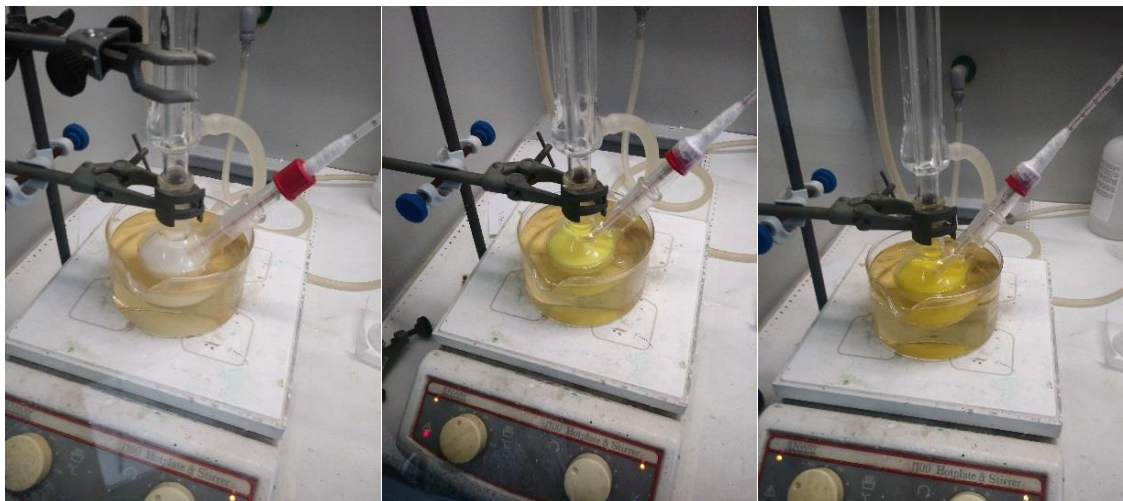


Figure 20 (left), before heating. Figure 4b (centre), few minutes after heating. Figure 4c (right), end of process.

4.2.3 Mixed synthesis.

In prior experiments in our lab there have been trials, with different doping methods than the one exposed in this paper (see 4.2) and calcination at 350°C. The doping methods were through ultrasounds [14].

After XRD and TEM tests, the CdS doped with Cu was contaminated with CdCO₃. Since the results of hydrogen production were better than other trials, an experiment to test a mixed of both compounds was made. The process was as follows:

1. 0.5g of CdS, produced through another method, are weighed. In the first trial Cd(NO₃)₂ 4H₂O and urea were weighted to get a 50:50 mass percentage of CdS and CdCO₃.
2. These compounds were mixed in a solution of 50ml of ethylenediamine in the reactor.
3. The reactor then was introduced into the hydrothermal furnace assisted by microwaves, heated up to 150°C during 30 min and then cooled down.
4. Once cooled, it is centrifugated and washed twice with H₂O. Then grinded and kept in an appropriate container.

4.3 Doping through Photodeposition

Attending to prior researches [13, 14, 15], adding some metals to the catalyst and enhance its efficiency. In this work studies with Cu doping through a photodeposition process were exposed. There are two slightly different methods that have been used.

4.2.1 Percentage calculations

The equation is stated as follows:

$$m(\text{Cu}) = \alpha \cdot m(\text{CdS}) \quad (\text{eq. 8})$$

Where $m(\text{Cu})$ is the necessary mass of Cu, $m(\text{CdS})$ the amount of mass chosen to go through photodeposition and α is the proportion of doping to be studied.

For the doping process the compound used was CuNO_3 .

4.2.1 1st Photodeposition of doped sample

In this process we used a transparent reactor, with 500mL of solution, which is put into a closed container connected to a purge gas (N_2) which is let at a flux of 100mL/min. The whole process is as follows:

1. 16 g of Methanol were measured and then the volume was completed with H_2O till 500mL.
2. 0.5 g of CdS were weighted and added to the reactor, with stirring.



Figure 21. Reactor without jacket. The solution was already poured in. This is before photodeposition.

3. The reactor is then taken into the wooden cage, completely covered with aluminum to avoid natural light.
4. The reactor is let there, with constant N_2 flux and stirring, for 30min

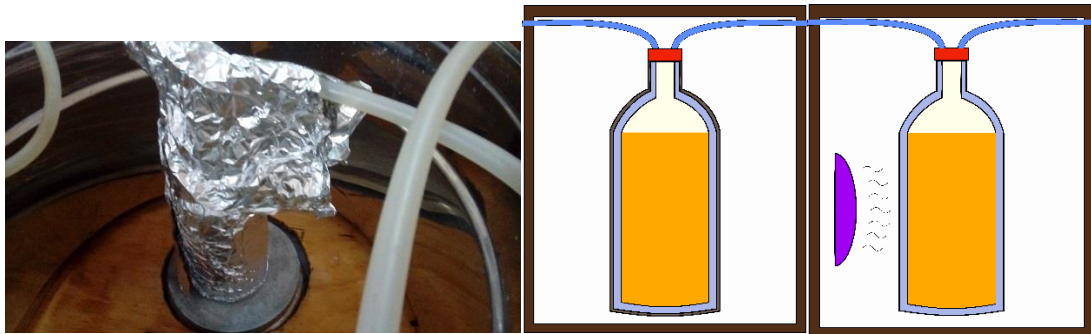


Figure 22 a. (left) Photo of covered reactor inside the cage. 22 b (center) 30 min of dark. 6c. (right) 2h of UV.

5. After that time the suitable amount of Cu is added. For that, CuCO_3 was used, calculating through the necessary amount of Cu mass percentage in relation to CdS. 0.5%, 1% and 2% were tried.
6. Once CuCO_3 was added the aluminum sheet was removed and the UV lamp was lighted for 2 hours. Usually, at the end the solution takes a darker color than usual, like a dark green.



Figure 23. Solution after photodeposition.

7. It was then centrifugated and washed once with water, avoiding natural light as much as possible. After being dried it was grinded and kept in an appropriate container.

4.2.2 2nd Photodeposition doping

In the process we used a transparent reactor, with 200mL of solution, and this time with the jacket. It was then put into the closed container connected to the purge gas (N_2) which was let at a flux of 100mL/min the whole process, which was adapted to the new volume. The whole process is as follows:

1. 6.408 g of Methanol were weighted and then the volume was completed with H_2O up to 200mL.

- 0.3 g of CdS were weighed and added to the reactor, with stirring.

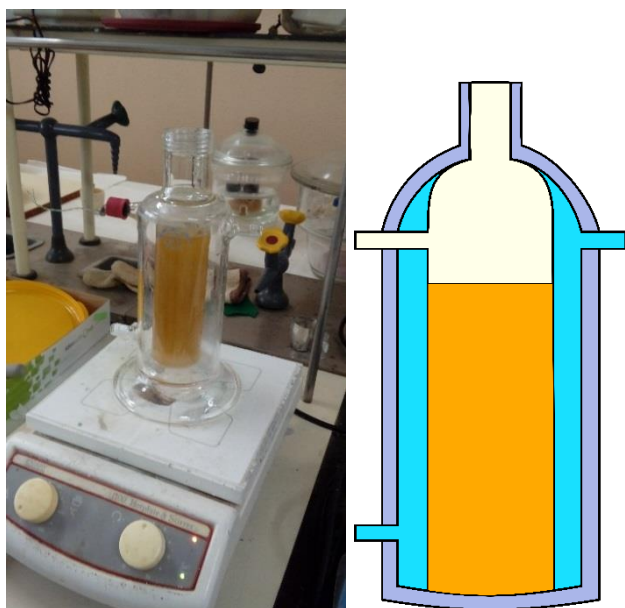


Figure 24. Reactor with the jacket for thermal controller. The color looks different due to ambient light.

- The reactor was then taken into the wooden cage, completely covered with an aluminum sheet to avoid natural light.
- The reactor is let there, with constant N_2 flux and stirring, during 30min.

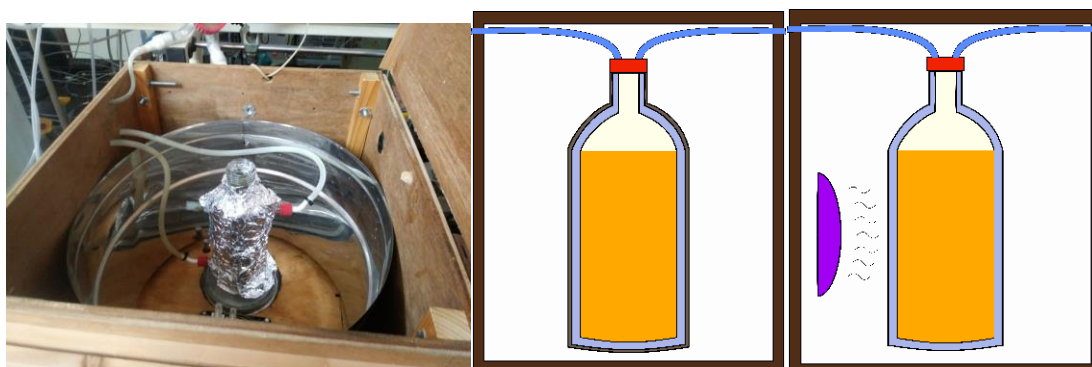


Figure 25 a. Photo of covered reactor inside the cage. 6b 30 min of dark. 6c. 2h of UV.

- After that time the appropriate amount of Cu was added. For that, $CuCO_3$ was used, calculating through the necessary amount of Cu mass percentage in relation to CdS. 0.5% and 1% were tried.
- Once $CuCO_3$ was added the aluminum sheet was removed and the UV lamp was lighted during 2 hours. Usually, at the end the solution takes a darker color than usual, like a dark green.

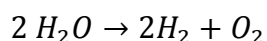


Figure 26 a and b. Typical color after photodeposition.

4.3 Photocatalysis

4.3.1 Process

Photocatalyst in our case is a reaction that consists in the splitting of water into molecular hydrogen and molecular oxygen, with the specific purpose of getting hydrogen.



This process is not spontaneous and needs energy to drive the reaction (read 2.1). Visible and UV light are used in this process to do so, trying to reproduce natural light conditions.

To reproduce that we take the reactor with catalyst solution inside it to be irradiated with the light from the lamps. The gases produced were removed through the tube with the purge gas up to stable levels of hydrogen were reached, then the lamps were on.

Specifically, the process goes as follows:

1. As in a typical common in Water Splitting process, sacrificial reagents were used in the reaction. In this case, 5.463g of Na_2S were dissolved in 100 mL of H_2O with stirring.
2. 6.302g of Na_2SO_3 were added into the reactor washing with water to drag it from the walls of the reactor. Stirring is kept.
3. 0.2 of the catalysts were weighted and water was added up to an amount of H_2O is 200mL. Stirring is kept.



Figure 27 a. (left) Sacrificial reagents. 12 b (right). Reactor after sacrificial reagents are poured. It gets transparent after enough stirring.

- The reactor was taken into the cage and connected to the tubes of the thermal control and gases, the spectrometer set at 120°C for correct functioning.
- The thermal control was put on and the reactor was closed with the upper lid, to avoid eyes damages to the operators.
- Purge gas was open and set at a flux of 100mL/min. Some bubbles should appear in the solution. When everything was checked to be fine, stirring was on and the cage was closed.
- The spectrometer controller was set on the computer and measures and records were set up.
- It was let at least 10 mins with flux of 100mL/min, up to the system looked stable.
- The flux was down to 10mL/min at least 10 min till it looked stable.
- Visible light was on and let for 100 min (sometimes it was let more time to check stability of production).
- Visible light was off, and UV was on during 100 mins more (sometimes it was let more time to check stability of production).
- Everything was stop, records are saved, and the equipment was turned off.

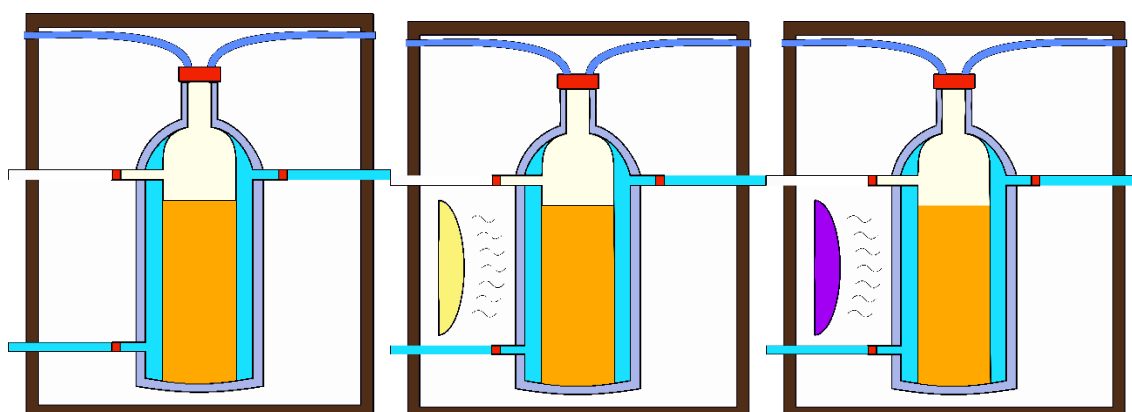


Figure 28 a. (left) Steps 8-9. 12b. (center) Step 10. 12c. (right) Step 11

- The solution was centrifugated, washed once with water, drilled and properly stored.

After photocatalysis samples for XRD were collected.

5. Results

En este capítulo se insertan los resultados obtenidos en el trabajo realizado, incluyendo los estudios de caracterización realizados en los servicios de la universidad: Difracción de Rayos X, XRD, y Microscopía Electrónica de Transmisión, TEM.

The results of the photocatalysis are compared and every step of the catalyst state is characterized so the research on the efficiency can continue.

5.1 Photocatalysis

The data of hydrogen production rate are given by the mass spectrometer in ppm per seconds, respect to the nitrogen flux. To better comparisons to other researches these are changed to $\mu\text{mol}/h\text{ g}$, i.e. μmol of hydrogen per hour and per gram of photocatalyst.

5.1.1 Comparison of efficiency of all tested catalysts

In general, all catalysts show higher efficiency under UV than visible irradiation.

Looking at figure 29, the catalysts in pink (hydrothermal synthesis), orange (reflux method 0.5%) and dark blue (reflux method 1%) are the ones with the highest production rates. The other catalysts were all synthesized through the hydrothermal method.

In the visible spectrum there are two rates of the hydrothermal method that look higher than the reflux method for the CdS non-doped, but for 1% is always higher.

In addition, comparing pure CdS prepared by the reflux method, though it looks like the doped will keep getting higher and the non-doped one will keep decaying, they coincide just at the end of the experimental process.

This can be better checked in the enlarged plots of figures 30 and 31.

The mixed method of synthesis does not show any improvement.

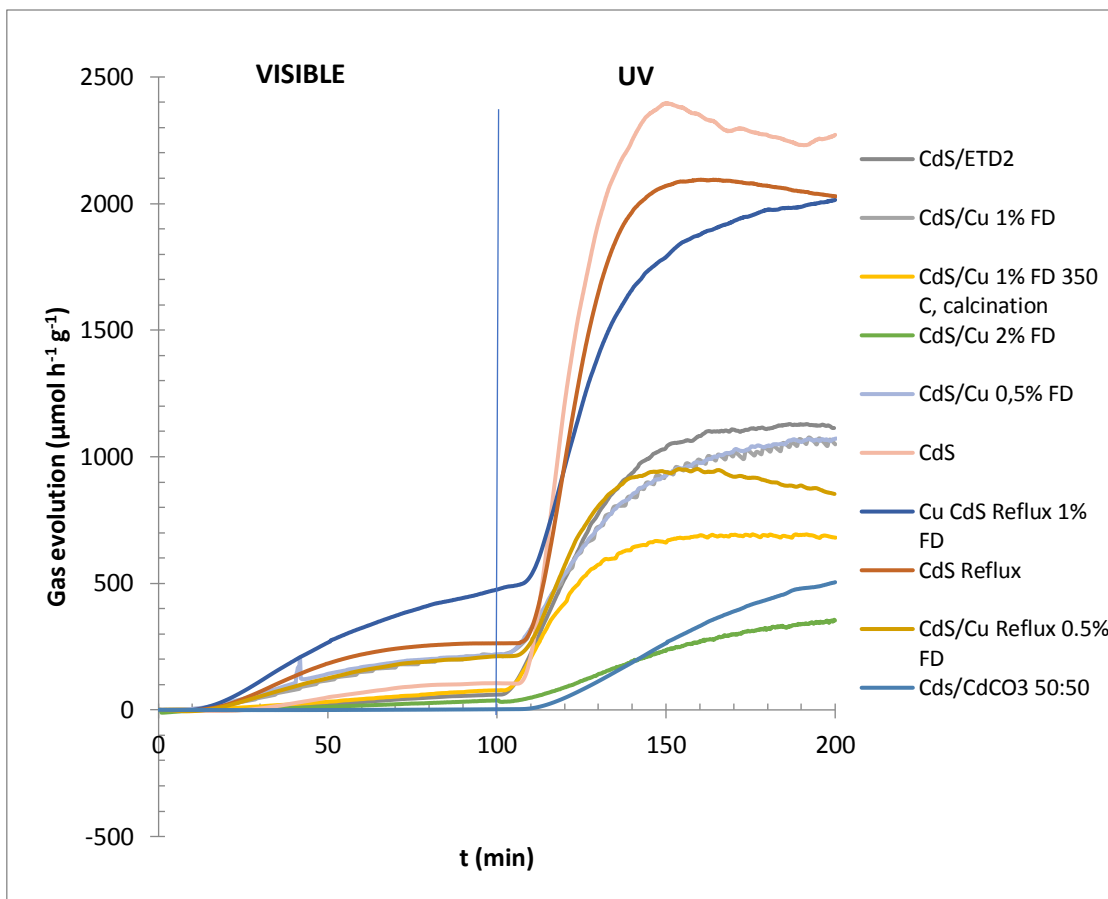


Figure 29. Hydrogen production under visible and UV irradiation.

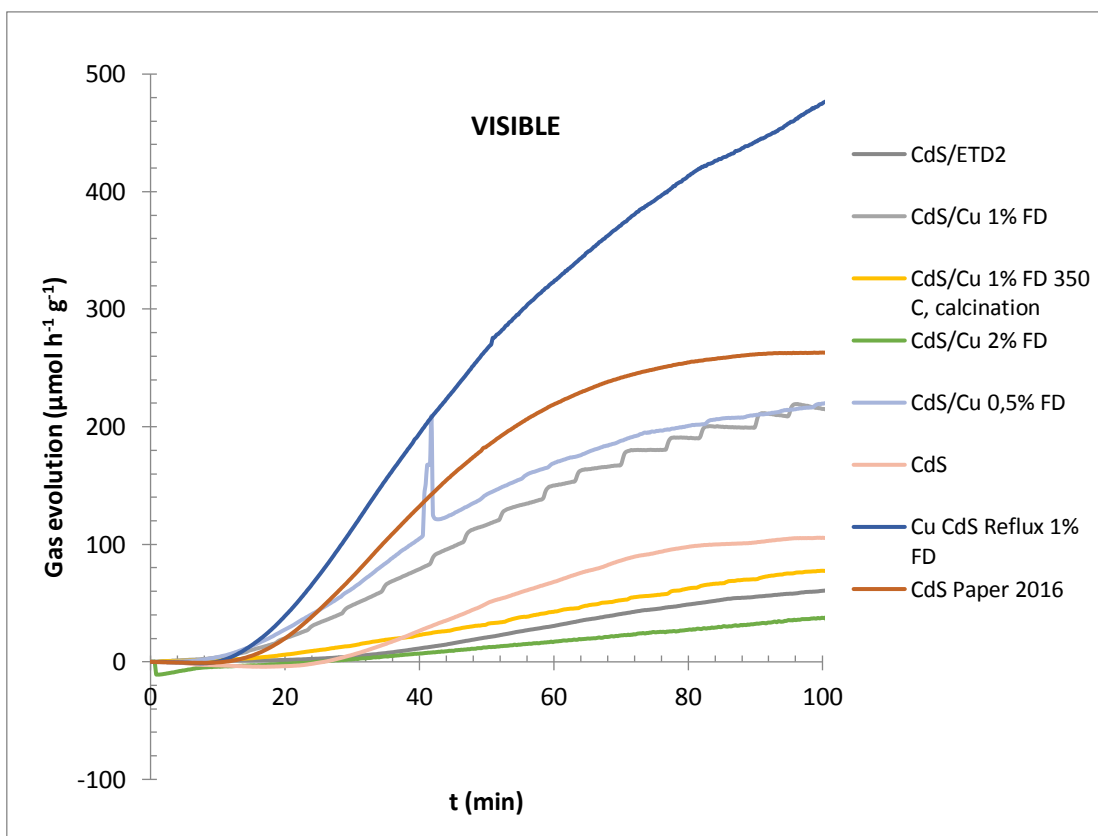


Figure 30. Hydrogen production under visible irradiation (enlargement of figure 29)

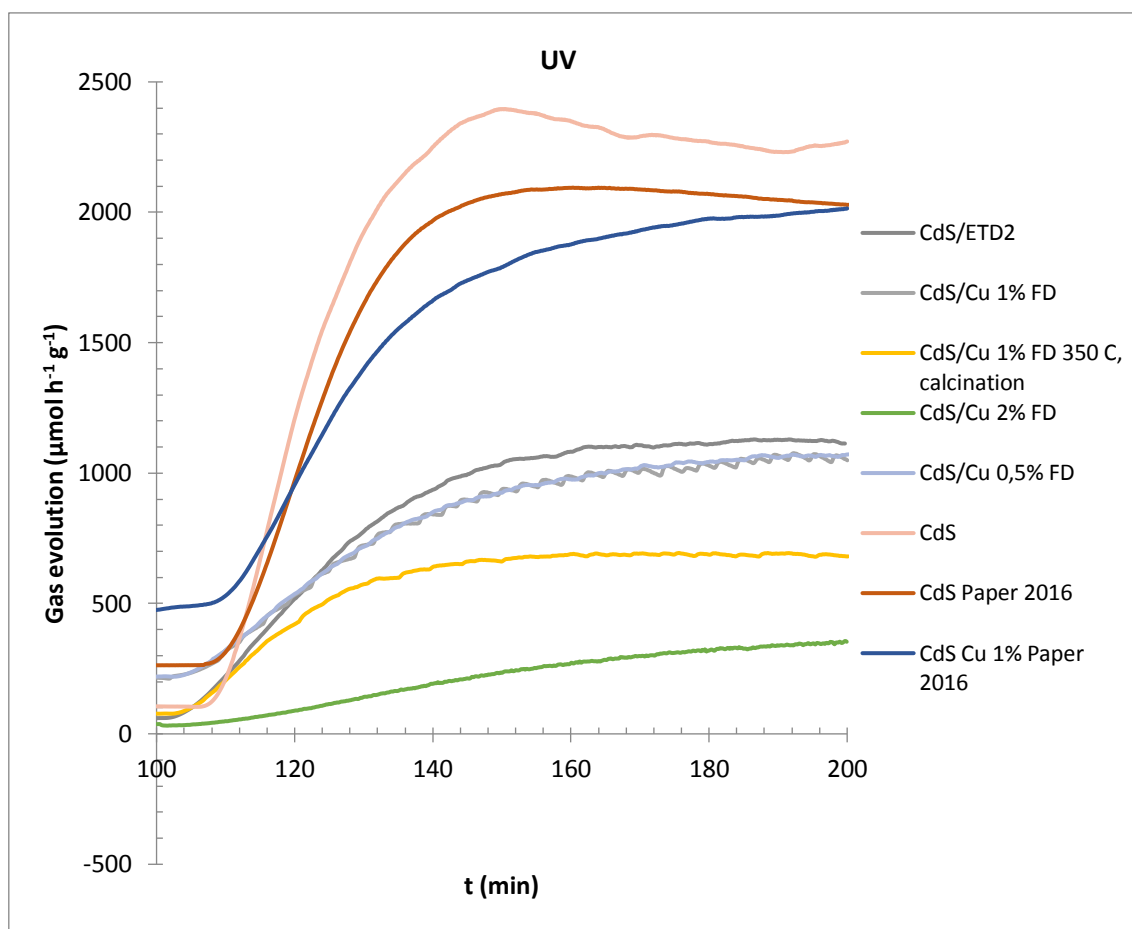


Figure 31. Hydrogen production under UV irradiation (enlargement of figure 29)

5.1.2 Comparison of long term photocatalysis

In figure 32 the comparison for long term experiment of photocatalysis under visible and UV radiation is shown. There is a slight tendency to decay with time. It is normal for catalysts to lose efficiency with time.

For the one with the 2% doping, even if it is a low production, it seems to completely stabilize through time, without tendency to decay.

If we compare only the ones with 1% in a short time (figure 33) we can see that the calcinated one is less efficiency but stabilize sooner. Also, the repetition is less efficient than the one with the first run.

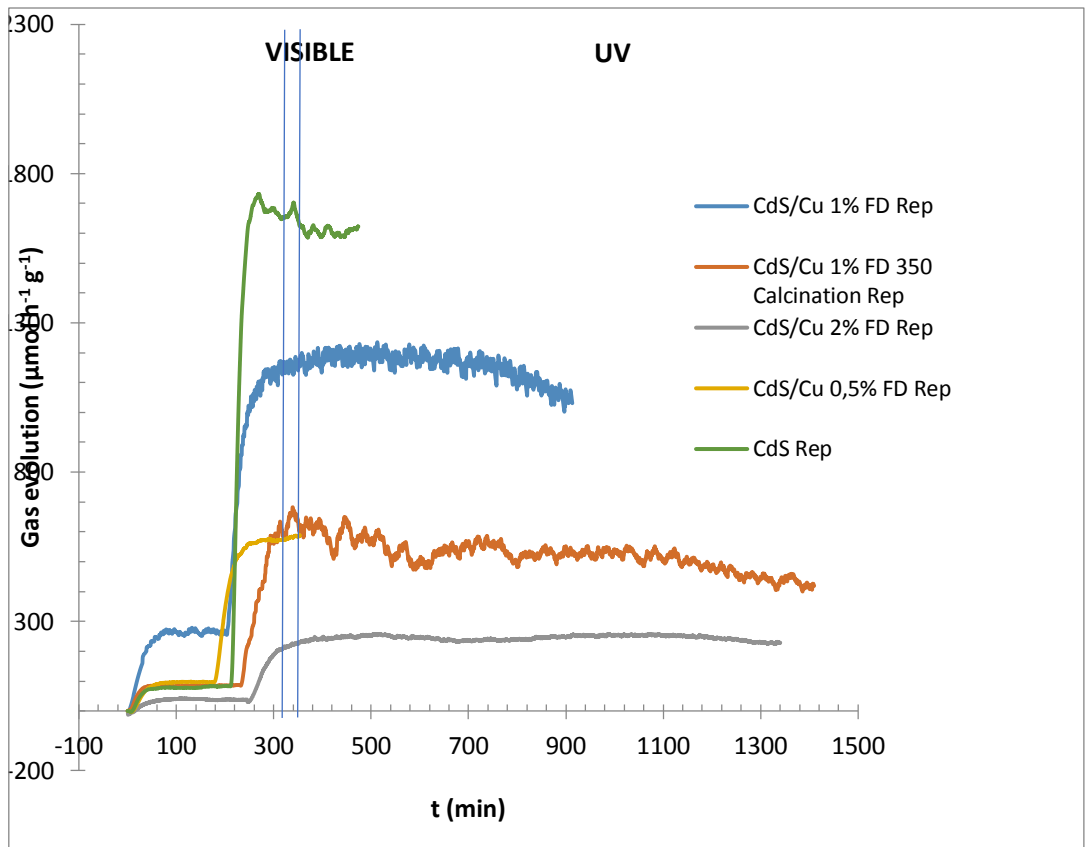


Figure 32. Long term experiments of photocatalysis under visible and UV radiation.

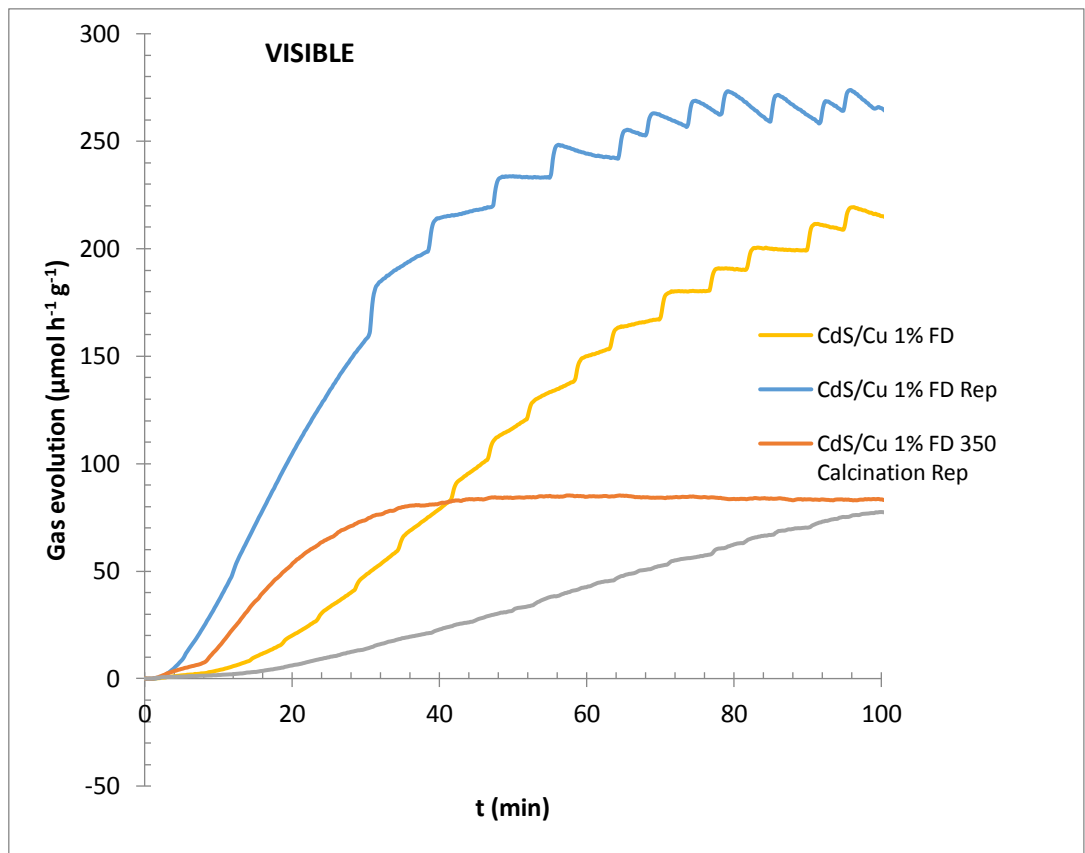


Figure 33. Long term experiments of photocatalysis under visible radiation (enlargement of figure 32)

5.2 Characterization

X Ray Diffraction (XRD) and Transmission Electronic Microscopy (TEM) tests were done to characterize the photocatalysts.

5.2.1 XRD

The different samples were studied by XRD to check the purity of CdS and the effect of doping with Cu and its oxidation state.

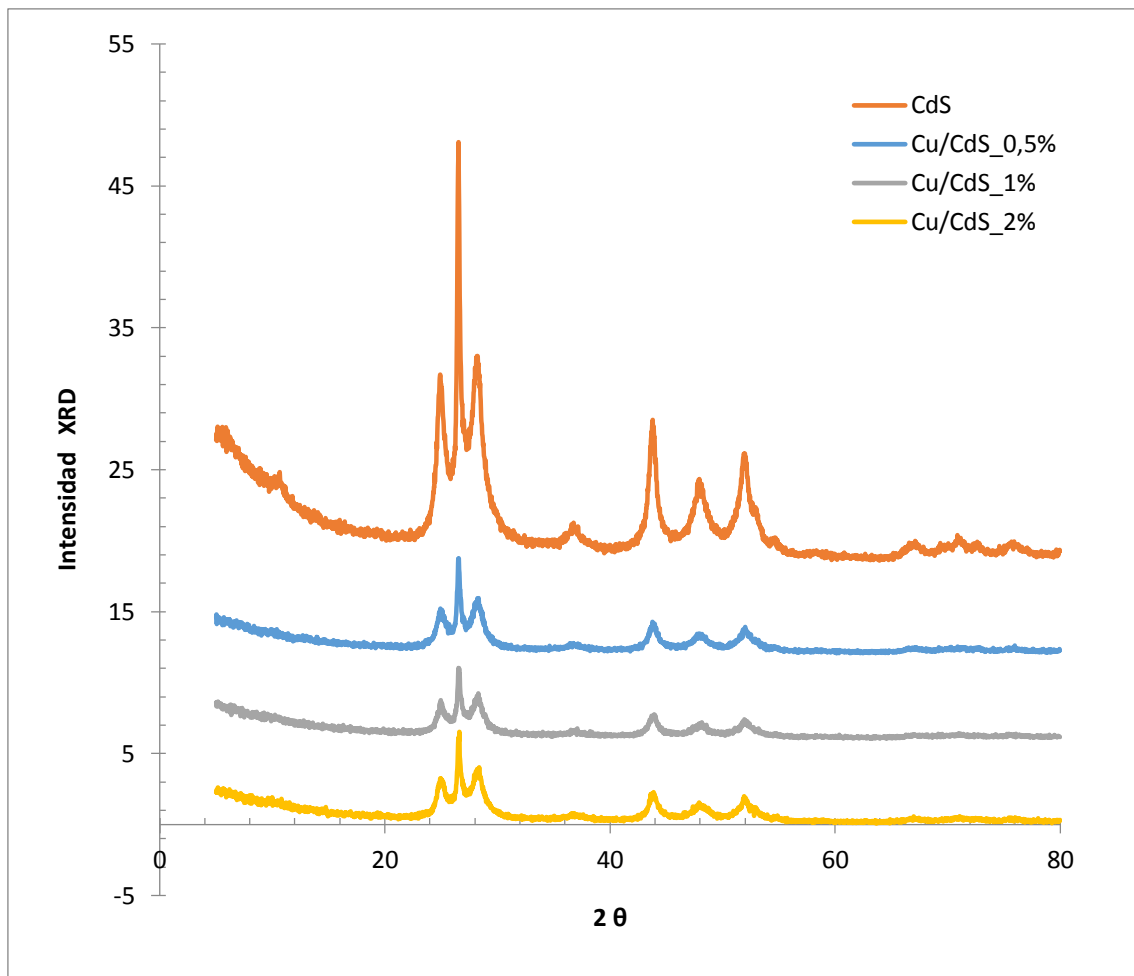


Figure 34. Cu/CdS measurements of XRD made by SEGAI, a service attached to the University of La Laguna. Intensity has arbitrary units.

The XRD patterns show the purity of CdS (single phase). The positions of the peaks are not affected by the photodeposition process and no additional phases are observed in the patterns.

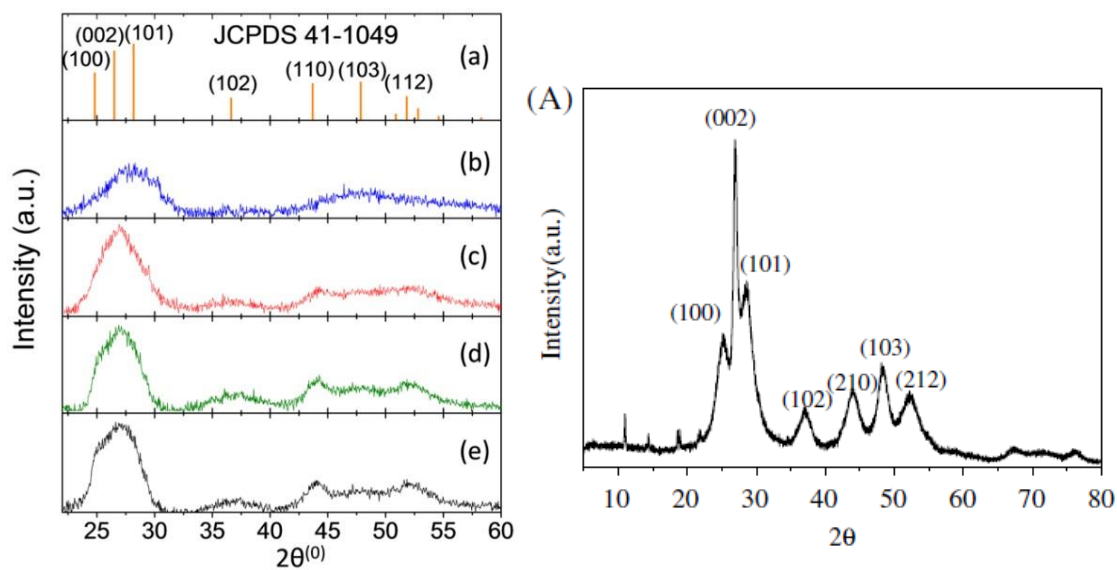


Figure 35. a (left) [17] JCPDS 41-1049 [17] b (right) [8] Sample spectra for CdS

5.2.2 TEM

TEM, due to overcharge of work on the University Services, only was measured the sample of 1% Cu doped CdS.

The results obtained from the tests made, are shown in figure 36.

Element	Peak Area	Area Sigma	k factor	Abs Corr.	Weight%	Weight% Sigma	Atomic%
S K	2927	104	0.959	1.000	17.79	0.64	40.64
Cu K	1312	62	1.393	1.000	11.58	0.54	13.35
Cd L	6180	180	1.803	1.000	70.63	0.84	46.01
Totals					100.00		

Table 1. TEM data

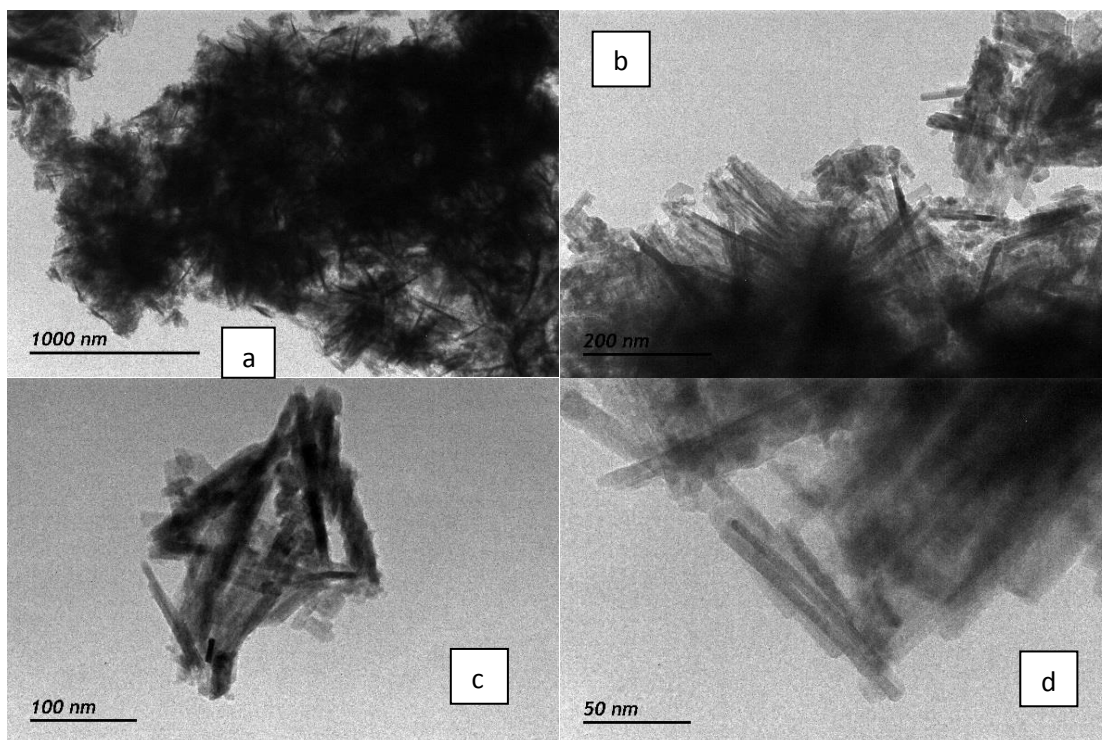


Figure 36. Different photos of the pictures from TEM test.

Strands are observed in the TEM pictures. Sizes seem to vary from 50 micrometers to 100. The strands show hexagonal section.

The percentage of Cu is higher than expected due to a grid of Cu was used in the TEM experiments. In all samples, the atomic proportions of Cd and S are similar, which coincide with the expected results for CdS.

6. Conclusions

En este capítulo se presentan brevemente las conclusiones extraídas de los resultados del capítulo 5 y se propone continuar a partir de ellos.

This work has included from synthesis production to doping and photocatalysis experiments. All equipment had been kept in used or was checked by technicians before it was used in the experiments.

Synthesis methods affect hydrogen production for CdS as catalyst in general. This is probably due to changes in the crystalline structure and morphology. Crossing data of samples prepared by different synthesis methods could help determine the optimum parameters.

CdS obtained by reflux method is in general more efficient than those obtained by the hydrothermal method. The Pure CdS prepared by the hydrothermal method shows better response under the UV irradiation, which was not expected since other runs of the experiment did not show this improvement against the same doped compounds (comparing to the doped ones of the same compounds). The synthesized compounds had been a few months in storage, in a closed container not exposed to light. An experiment comparing the materials just prepared and long time after preparing the synthesis could be run to check if the compound may be affected by store period.

Long term experiments in general seems to lower efficiency for any compound but stabilize earlier. Analyzing this is an important issue to get durable catalysts.

The mixed synthesis did not show any special results, so different amounts of mixing should be tried.

The calcination did not show improvement. It had not been checked with the reflux method synthesis yet.

This work needs to be continued in order to achieve optimum conditions for the hydrogen production.

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Figures note:

If not acknowledge, it is a picture made or taken by Ruth de la Pinta Madico

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