



## Photo-Assisted Synthesis of GO/ZnO Nanocomposites for the Production of Photocatalytic Hydrogen

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## ABSTRACT

In this study, zinc oxide was synthesized by the precipitation method. Graphene oxide (GO) was prepared by oxidation of graphite powder using a microwave pretreatment. This GO was used for the modification of the photocatalytic properties of ZnO. Fixation of particles was carried out using a photoassisting technique by visible light irradiation. Characterization of the material consisted in morphology, crystalline structure and optical properties and these were performed by XRD, SEM, BET and UV-Vis spectrometry, respectively. Photocatalytic evaluation of the material towards the water splitting reaction was followed by gas chromatography, using a metal halide lamp of 250W as a light source in a quartz-sealed photocatalytic reactor, obtaining a production of  $1,200 \ \mu molH_2/g$ , showing an enhanced photocatalytic activity compared to ZnO.

Keywords: graphene oxide, photo-anchoring, hydrogen production, ZnO/graphene oxide

## 1. Introduction

In recent decades, world population has doubled, which has led to an increased energy consumption. The current lifestyle of humanity depends on energy coming from fossil fuels such as natural gas, methane and coal. Therefore, in order to alleviate the problem of future energy demand, renewable energies, such as solar energy, biofuels and nuclear energy, must be implemented, because fossil fuels are finite [1].





From today's alternative energy options, hydrogen is considered a promising energy carrier derived from solar energy, and the use of hydrogen as an energy vector, especially in the automotive sector, has awaken the interest of hydrogen in the world's energy arena, because it is clean, renewable, is abundant in nature and in combination with fuel cells are highly efficient for power generation systems. These are the reasons why several alternatives have been proposed for their production in an environmentally responsible way using green technologies [2–5]. Since the dissociation of the water molecule by photoelectrochemistry was reported, the production of H<sub>2</sub> by photocatalysis has been of great scientific interest [6] and the study of semiconductor materials with photocatalytic materials aiming the water splitting reaction for the production of hydrogen include BiVO<sub>4</sub> [7], TiO<sub>2</sub>[7,8], WO<sub>3</sub> [9], CdS [8], C<sub>3</sub>N<sub>4</sub>[10], and ZnO [11,12].

ZnO is, like TiO<sub>2</sub>, one of the most studied photocatalysts due to its low toxicity, thermal stability and high efficiency. However, one of its most important limitations lie in the photocorrosion that this material presents. Furthermore, generally speaking, oxides exhibit a low charge mobility and ZnO is not the exemption. Therefore, it is necessary to develop a material or a combination of materials that will extend recombination times to compensate for the low density of ZnO carriers. Recently, different research aiming to improve photocatalytic properties of ZnO has emerged and proposed several strategies in an attempt to solve this problematic, such as the synthesis of ZnO nanorods [13], heterojunctions with other semiconductors [14], doping and inclusion of carbonaceous materials [3,15], including graphene.

Graphene, is a two-dimensional flat monolayer of carbon atoms bonded in a honeycomb structure, which exhibits very interesting electronic properties, such as zero band gap and high conductivity [16]. Recently, the incorporation of metal oxides in graphene sheets has been reported to obtain composite photocatalysts [3,17,18].

Based on the methodology proposed by Williams et al. in 2008 [19] for the assisted photo anchoring, this work proposes the use of visible light irradiation to anchor ZnO particles on the surface of GO, which according to the literature, the combination of GO with an appropriate photocatalyst such as ZnO may result in a significant improvement of the material photocatalytic activity. Furthermore, it is worth to mention that up to date, studies conducted on this material have been mainly focused on the photocatalytic degradation of pollutants in water.

#### 2. Methodology

#### 2.1. Synthesis of graphite oxide

Graphite oxide was synthesized from graphite powder using a modification of Hummers method [20,21]. 1 g of graphite was exposed to a microwave pretreatment [22] during 15 s, immediately after, a concentrated solution of  $H_2SO_4$  / $H_3PO_4$  with a 9:1 ratio was added (43.2 mL and 4.8 mL, respectively). This mixture was kept under magnetic stirring and in an ice bath (4°C) for 4.5 h. After this time 6 g of KMnO<sub>4</sub> were added under constant stirring for 3 h, finally a solution of  $H_2O_2$  (12 mL) and 10% HCI (13 mL) was added





by drip irrigation while keeping the mixture under stirring for 0.5 h and under an ice bath due to the exothermic nature of the reaction [20]. Next step was washing and filtering with three distillated water, assisted by a vacuum pump until the residuals of acid and potassium permanganate present in the mixture have been removed, once completed this step GO was dried in a muffle furnace at 65°C.

## 2.2. ZnO Synthesis

In order to prepare ZnO particles, the precursor solution was first prepared by a precipitation method. 100 mL of 1.5 M Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O solution was added dropwise into 126 mL of 2.5 M NH<sub>4</sub>HCO<sub>3</sub> solution under vigorous stirring at 45 °C in a water bath for 30 min to produce Zn(HCO<sub>3</sub>)<sub>2</sub>. The product was filtered, washed, and rinsed with deionized water and 95% ethanol. In the last stage, the Zn(HCO<sub>3</sub>)<sub>2</sub> product was dried in an oven at 100 °C for 24 h, followed by calcination at 600 °C for an additional 1 h.

## 2.3. ZnO anchoring in graphene oxide

In order to synthesize the GO/ZnO composite, a certain amount of GO and ZnO (as required to obtain 10 % by weight of graphene oxide (GO) was suspended in an aqueous solution at 30% ethanol and using an ultrasonic bath (Branson 2510) at a frequency of 40 kHz for 15 min, separately and simultaneously, the ZnO was also exposed to ultrasound vibrations to obtain a homogeneous suspension. After 15 min the GO suspension was poured into the ZnO suspension, while keeping a continuous exposure to sonication until 40 min. The sample was placed within a photoreaction system under visible light radiation of a metal halide lamp (250 W) and under constant stirring for 24 h, the resulting solution was dried on a hot plate at 80°C for 12h.

## 2.4. Characterization

In this study the crystalline phase present in each of the synthesized materials was determined by the x-ray diffraction technique using a Phillips Xpert Pro diffractometer, equipped with a Cu-k $\alpha$  radiation ( $\lambda = 1.54056$  Å). Diffraction patterns were obtained with a 2 $\theta$  sweep angle of 5° to 90°, with a step size of 0.05. The absorption and diffuse reflectance spectrum of the materials were obtained with a UV Visible Evolution 220 Thermo-spectrophotometer equipped with integration sphere. The BET surface area was determined with an Autosorb-1 brand Quantachrome using the N<sub>2</sub> adsorption technique from 0.05 to 0.3 relative pressure (P/P<sub>0</sub>). Morphology of the samples were examined by field emission scanning electron microscopy (SEM) in a JEM-2200FS, where the sample was eposed to a beam of electrons generated from a tungsten filament, to minimize energy losses or deviations of the beam, the column must have an ultra-high vacuum of 10<sup>°</sup> Torr [21].

## 2.4.1. Photocatalytic Evaluation

The photocatalytic activity was evaluated based on the performance of the material towards the production of hydrogen for the dissociation of the water molecule, using as a





250W metal halide lamp as a source of energy and 2% methanol as a sacrifice agent. The reaction was monitored by gas chromatography using a Perking Elmer Clarus 580 gas chromatograph, taking samples at time intervals of 1h with 8 repetitions.

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### 3. Results and discussion

#### 3.1. X-ray diffraction

The crystalline structure of the samples was analyzed by X-ray diffraction. Figure 1 shows the diffraction patterns of ZnO, the synthesized graphene oxide (GO) and the GO/ZnO nanocomposite. The diffraction pattern of GO presents a signal at  $2\theta = 10^{\circ} = 10^{\circ} \cong 8.842$ Å, which corresponds to graphene oxide. The diffraction pattern of ZnO shows characteristic peaks of the Wurtzite phase with a crystallographic record of 00-080-0075, in which an average crystallite size of 16.31 nm was estimated by means of the Scherrer's equation [23]. In the GO/ZnO nanocomposite diffractogram it can be clearly observed the fading of the signal corresponding to graphene oxide showing mainly the characteristic peaks of ZnO, while maintaining the amorphous phase associated with graphene oxide, which shows that the presence of GO does not promote the formation of new crystals or changes in the preferential orientation of ZnO



Fig. 1 X-ray diffraction patterns of GO, ZnO and GO/ZnO samples

#### 3.2. Scanning electronic microscopy

Fig. 2 a, b and c show images of scanning electron microscopy for the GO/ZnO sample, where it can be seen that ZnO anchoring occurred only in certain places of GO, particularly on the edges, as well as a possible sintering of ZnO particles as shown in Fig. 2d, which probably be the cause of a poor distribution of these particles over leaves of GO. Furthermore, a scaly morphology can also be seen on some portions of GO, which was presumably caused by the exfoliation process.







Fig. 2 SEM micrographs of the GO/ZnO composite.

## 3.3. UV-Vis Spectroscopy diffuse reflectance

Figure 3 presents the absorption spectrum of ZnO, GO and GO/ZnO samples obtained by the diffuse reflectance technique where ZnO shows a maximum absorption within the UV range at approximately 400nm. While, GO shows absorption in almost all the evaluated spectrum, so it can be assumed that the level of oxidation of the material is low [24]. On the other hand, the GO/ZnO behavior shows the limit of its absorption spectrum at 460 nm within the visible range. These results agree well with those reported in the literature for GO and ZnO nanocomposites under a similar composition of the nanocomposite under study [25].



Fig. 3 UV-vis absorption spectra of GO, ZnO and GO/ZnO samples.

Estimation of the band gap energy was performed using the Tauc plot by means of the Kubelka-Munk function and this is presented in Figure 4. In this figure the numerical value of the band gap energy for ZnO and GO/ZnO is shown in Figure 4a) where the direct transition of both materials is presented. Here, ZnO shows an Eg of 3.22 eV [26] that agrees values found in the literature, where an Eg value similar to that of TiO<sub>2</sub> is considered. Otherwise, in plot 4b) the determination of Eg by indirect transition of ZnO and GO/ZnO composite samples presented values of 2.77 and 3.11 eV, respectively. This reduction in the band gap, according to the literature can be attributed to the inherent properties of the GO for its character of electron trap [14].



Fig. 4 Estimation of the direct and indirect Eg by the Kubelka-Munk method.





#### 3.4. BET Surface Area

Figure 5 shows the adsorption isotherms of the GO/ZnO composite, where a surface area of 31  $m^2/g$  was determined and presenting a type III isotherm, without porosity.



Fig. 5 BET Adsorption isotherms for samples GO, ZnO and GO/ZnO.

## 3.5. Photocatalytic Evaluation.

The incorporation of GO to ZnO generates interesting benefits in terms of photocatalytic properties. This is shown in Figure 6 where the performance towards the hydrogen production of each material (GO, ZnO and GO/ZnO) is presented in terms of  $\mu$ molH<sub>2</sub> as a function of time. Results indicate a hydrogen production of of 127, 50 and 156  $\mu$ mol/g·h for GO, ZnO and GO/ZnO samples, respectively.

Furthermore, ZnO generates small amounts of hydrogen because its range of absorption of photons is in the UV range, due to this the density of charge carriers, is poor which results in a low photocatalytic activity. Regarding the performance of the GO/ZnO composite in the dissociation of the water molecule, it shows a significant improvement compared to its precursors, which can be associated to the surface interaction between the ZnO and the GO sheets. According to the literature, GO acts as an electron collector and presents a high charge mobility, a characteristic that is attributed to its two-dimensional profile, coupled with the conjugation of the  $\pi$  bond [27].







Fig. 6 Photocatalytic evaluation of GO, ZnO and GO/ZnO samples.

## 4. Conclusions

- It was possible to synthesize ZnO particles with a crystallite size of 16.31 nm by the precipitation method.
- GO was obtained by ultrasonic exfoliation.
- A GO/ZnO composite was produced by photo-assisted anchoring by visible light.
- The 400nm to 460nm shift from the absorption range in the GO/ZnO composite to the visible was achieved.
- A bandgap decrease was obtained at a less energetic level of 3.22 to 2.7 eV.
- The photocatalytic properties of ZnO in the production of hydrogen were improved by the addition of 10% by weight of GO, obtaining a production of 1250 µmol/g of hydrogen after 8 hours.

Las propiedades fotocatalíticas del ZnO en la producción de hidrógeno se mejoraron mediante la adición del 10% en peso de GO, obteniendo una producción de 1250  $\mu$ mol/g de hidrogeno en 8 horas.

## 5. References

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