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Synthesis and characterization of Bi_2O_3:Gd for hydrogen production under visible light.

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ABSTRACT

Photocatalytic water splitting is one of the cleaner processes for molecular hydrogen and oxygen production using semiconductor. For better utilization of solar spectrum and complete redox for water splitting applications, it is required to have a semiconductor which is photoactive in visible region. The Bi_2O_3:Gd photocatalyst was successfully synthesized by Pechini method. The physical and chemical properties of as-prepared samples were characterized based on XRD, SEM, BET and UV-vis. Bi_2O_3 is an important inorganic functional material. It has got much attention due to its unique electrical and optical properties, which lead to its extensive usage in catalysis. Also, it is a promising visible-light-driven photocatalyst whit a narrow bandgap (2.6-2.9 eV). It has been proved that β-Bi_2O_3 had the higher photocatalytic activity than α-Bi_2O_3 but only a few researches on β-Bi_2O_3 have been reported due to the difficulty of synthesizing the metastable β-phase [3]. The β-phase was confirmed using DRX.

Keywords: Bi_2O_3; Photoelectrolysis; Hydrogen; Photocatalyst

1. Introduction

Production of cleaner energy using renewable resources and non-energy intensive process are in great demand to cater the present and future energy supply. Hydrogen gas served as low density and high energy content cleaner fuel, demonstrated as best alternative to fossil fuels for sustainable energy developments. Hydrogen as an important energy carrier in the future has a number of advantages. For example, a large volume of hydrogen can be easily

stored in several different ways. Hydrogen is also considered as a high efficiency, low polluting fuel that can be used for transportation, heating, and power generation in places where it is difficult to use electricity. In some instances, it is cheaper to ship hydrogen by pipeline than sending electricity over long distances by wire. However, the large-scale H_2 production is mainly based on fossil fuels splitting or water electrolysis, which has led to high energy consumption and severe environmental pollution. Since the pioneering work of Fujishima and Honda on semiconductor photocatalysis, the direct H_2 production via water splitting using solar energy has been extensively investigated as a promising way to meet the ever-growing global energy demands. Bi_2O_3 semiconductor photocatalyst has gained considerable attention due to its good absorption capacity (band gap of 2.8 eV) and found to be very good catalyst for environmental application as well as photocatalytic water splitting.

2. Material and methods

Reagents		
$Bi(NO_3)_3 \cdot 5H_2O$	Aldrich	98%
$Gd(NO_3)_3 \cdot 5H_2O$	Aldrich	98%
Ethylene glycol	Aldrich	>99%
Tartaric acid	E. Merck	99.5%
HNO_3	J.T. Baker	69-70%
Water	---	Deionized
NaOH	J.T. Baker	89%

To obtain Bi_2O_3 by the Pechini method, we used $Bi(NO_3)_3 \bullet 5H_2O$ and $Gd(NO_3)_3 \bullet 5H_2O$ as a precursor, tartaric acid as a chelating agent and ethylene glycol as a polymeric agent, $Bi(NO_3)_3 \bullet 5H_2O$ was dissolved in a 5% HNO_3 solution, with moderate agitation for 30 minutes to obtain a transparent solution of Bi^{+3}. On the other hand, a solution of tartaric acid was prepared, this solution was added dropwise to the Bi^{+3} solution to carry out the chelation of the metal in a 1: 1 molar ratio. To this mixture was added ethylene glycol in a 1:1 molar ratio (tartaric acid: ethylene glycol), the addition was made drop by drop to polymerize the previously formed complex. The mixture stirred for a period of 24 h and subsequently adjusted to pH 0.5 with NaOH at 25% with a potentiometer, until forming a dense sun. Through a reflux system, the formed sun was heated at 80 °C for 2 h and then at 105 °C for 2 h to achieve condensation and finally kept in slow agitation for 24 h. Later we proceeded to eliminate the remaining solvent using a rotaevaporator with a water bath at 90 °C to get the xerogel. The xerogel was dried at 95 °C for 2 h and subsequently the white solid has been pulverized and calcined in a muffle at 390 °C for 3 h, with a heating ramp of 2 °C min^{-1}.

3. Results and discussion

3.1. XRD

The diffractogram of figure 1 shows that the phase obtained from undoped Bi_2O_3 by the Pechini method is the monoclinic alpha phase, in the figure 2 when the Bi_2O_3 was doped with the gadolinium, we obtain a mixture of phases due to a transition in the crystalline structure of the material. Phase transition occurs from the monoclinic alpha phase to a tetragonal beta phase, as we can see in figure 2 this probably due to the rearrangement of the atoms when gadolinium is added to the catalyst, finally, in figure 3 we can see that we only have present the beta phase of the material, which has been reported as the most photoactive crystalline phase.

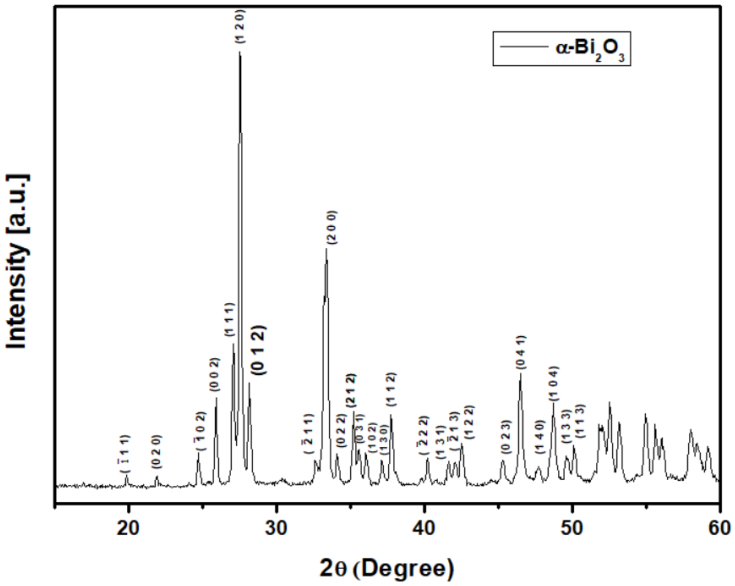


Figure 1. Diffractogram obtained by XRD of pure Bi_2O_3 without doping.

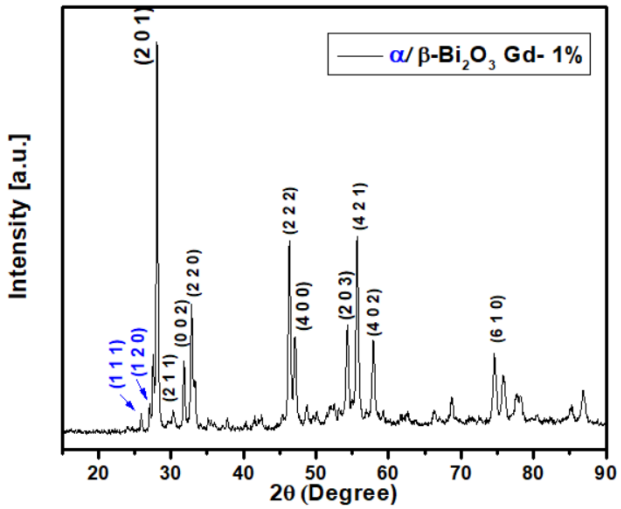


Figure 2. Diffractogram obtained by DRX of Bi_2O_3 doped with 1% gadolinium.

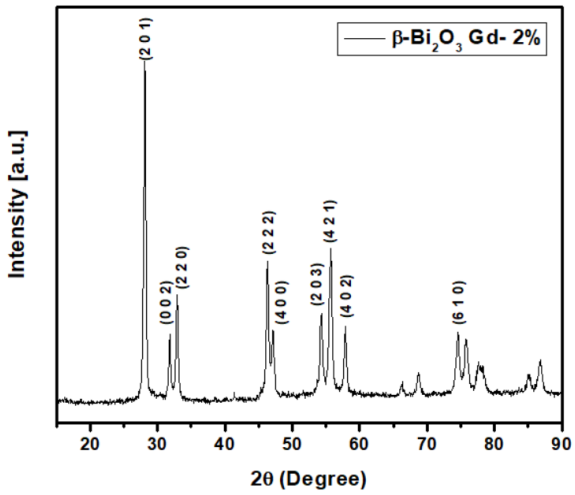


Figure 3. Diffractogram obtained by DRX of Bi_2O_3 doped with 2% gadolinium.

3.2. DRS Uv-Vis

It can be observed in figure 4 that when doping the material with gadolinium a change is obtained in the optical Bandgap of the material, the Bandgap obtained with the pure Bi_2O_3 is 2.95 and it is possible to reduce it to a value of 2.53 when doping with gadolinium.

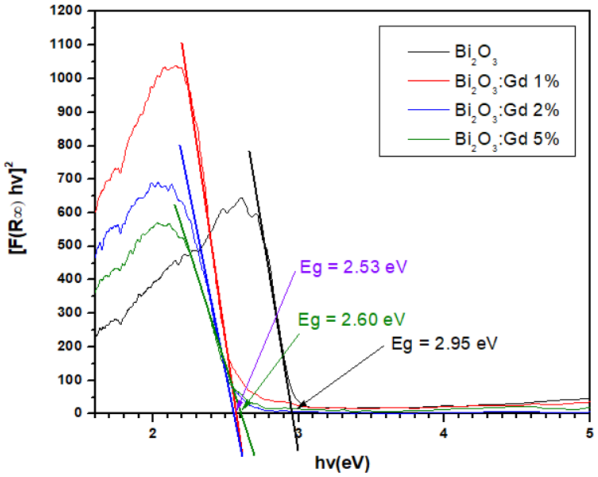


Figure 4. Calculation of optical Bandgap using the diffuse reflectance method Uv-Vis.

3.3. Scanning Electron Microscopy (SEM)- Energy Dispersive Spectroscopy (EDS).

In figure 5 we can observe the formation of bars and flakes of Bi_2O_3, the formation of these structures are characteristic of the synthesis method and the material, which have been previously reported. In the Energy Dispersive Spectroscopy results the presence of bismuth oxide was confirmed

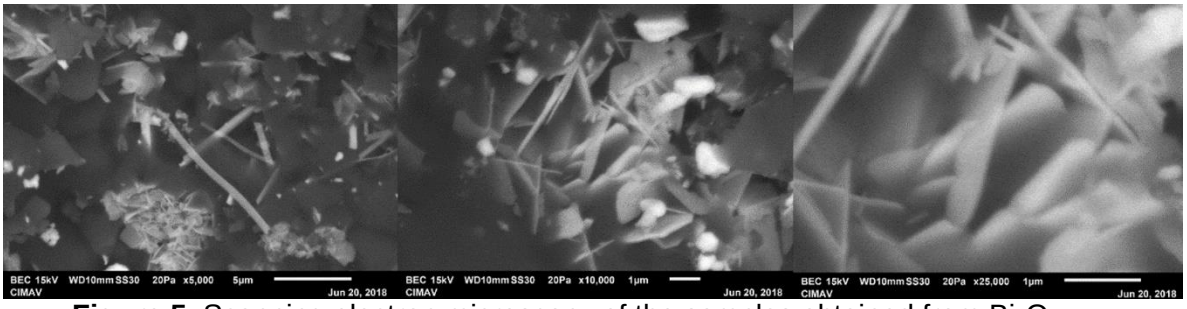
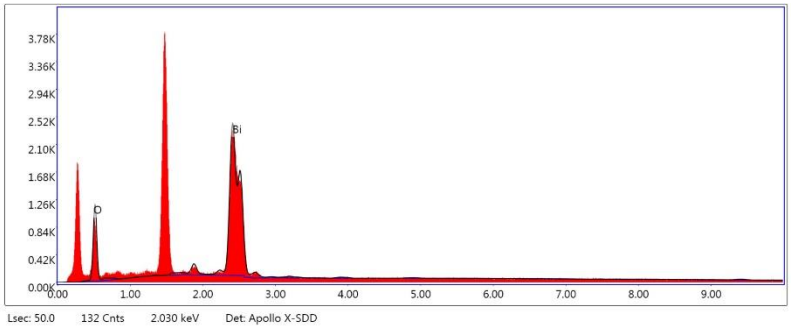
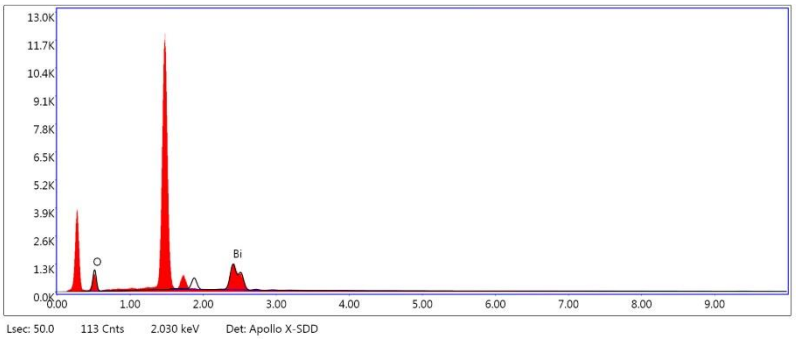


Figure 5. Scanning electron microscopy of the samples obtained from Bi_2O_3.



Element	Weight %	Atomic %
O K	38.89	89.26
BiM	61.11	10.74

Figure 6. Energy Dispersive Spectroscopy of the samples obtained from Bi_2O_3.



Element	Weight %	Atomic %
O K	26.89	82.77
BiM	73.11	17.23

Figure 7. Energy Dispersive Spectroscopy of the samples obtained from Bi_2O_3 with 1% Gd.

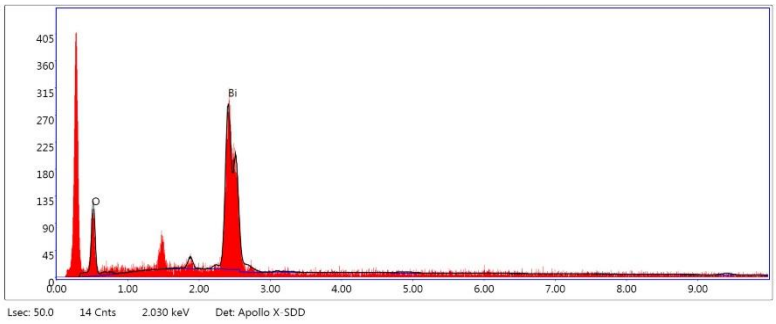
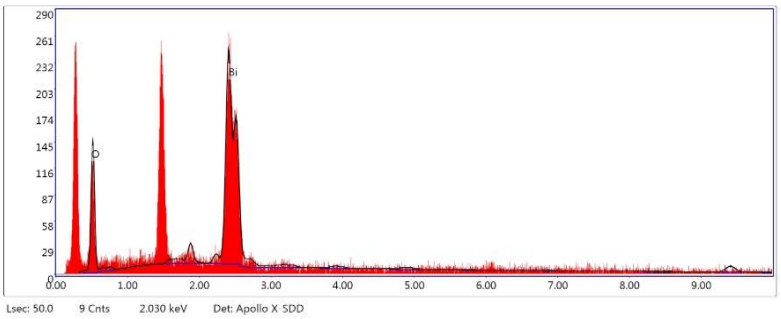


Figure 8. Energy Dispersive Spectroscopy of the samples obtained from

Bi_2O_3 with 2% Gd.



Element	Weight %	Atomic %
O K	29.86	84.15
BiM	70.14	15.24

Figure 9. Energy Dispersive Spectroscopy of the samples obtained from Bi_2O_3 with 2% Gd

3.4. N_2-fisisortion (BET)

Type IV isotherms were obtained which are characteristic of the mesoporous solids, this hysteresis cycle is due to the mesoporous filling process which is governed by capillary condensation phenomena, the hysteresis loops are type 3, which are obtained when working with pore agglomerates of parallel plates, which agrees with the micrographs obtained in MEB where the formation of flakes in the material can be seen, the Bi_2O_3 catalysts had a low specific area, they did not present a significant change in the pore radius, and an increase in the specific area was observed in the Bi_2O_3:Gd 5% samples.

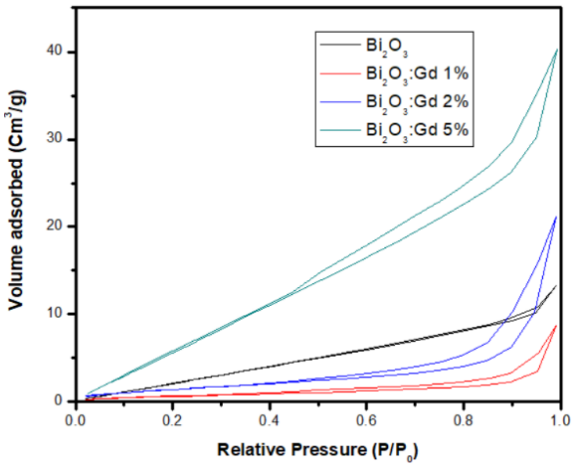


Figure 10. Nitrogen fisisorption isotherms of catalysts based on Bi_2O_3.

Element	Weight %	Atomic %
O K	32.87	86.48
BiM	67.13	13.52

	Bi_2O_3	Bi_2O_3:Gd 1%	Bi_2O_3:Gd 2%	Bi_2O_3:Gd 5%
Surface Area (m^2/g)	9.983	2.037	5.092	28.279
Pore Volume (Cm^3/g)	0.020	0.013	0.032	0.061
Pore Radius Å	15.441	15.440	15.291	15.243

3.5. Photocatalytic evaluation of hydrogen production.

It can be seen in the graphs that the material with the best performance with respect to hydrogen production was Bi_2O_3: Gd 2%, obtaining a considerably better performance than

that obtained with Bi_2O_3: Gd 1% and Bi2O3: Gd 5%, the doping of the gadolinium material favored the production of hydrogen. Hydrogen production was not obtained with the pure Bi_2O_3 catalysts.

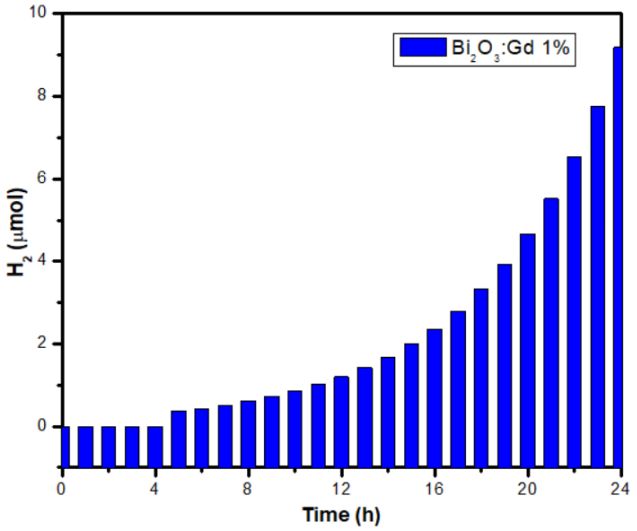


Figure 11. Photocatalytic evaluation of hydrogen production with Bi_2O_3 catalyst:Gd 1%.

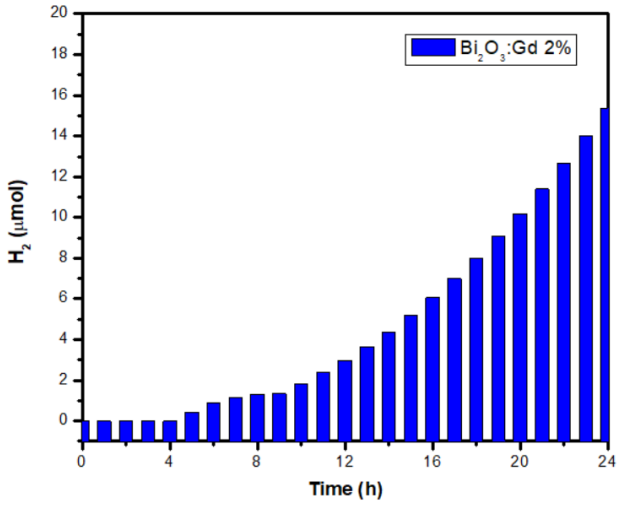


Figure 12. Photocatalytic evaluation of hydrogen production with Bi_2O_3 catalyst:Gd 2%.

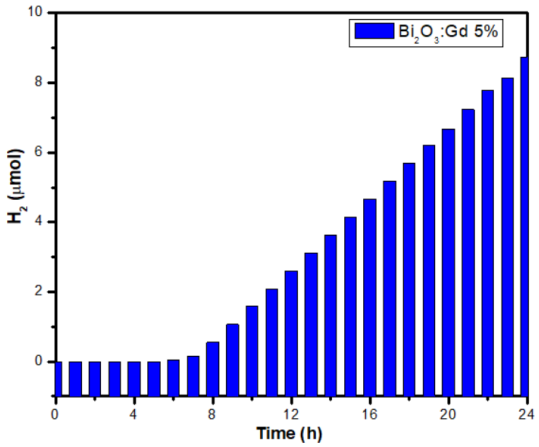


Figure 13. Photocatalytic evaluation of hydrogen production with Bi_2O_3 catalyst:Gd 5%.

3.6. Discussion

The addition of gadolinium at different percentages in the catalyst affects its optical and structural properties, causing a phase change due to a transition in the crystalline structure of the material. The phase transition occurs from the monoclinic alpha phase to a tetragonal beta phase, due to the rearrangement of the atoms as gadolinium is added to the catalyst. A reduction of the Bandgap in the doped materials was also obtained, since the Bi_2O_3 presents an optical Bandgap of 2.95 eV and when adding the gadolinium to the material, a reduction of the optical Bandgap is obtained up to a value of 2.53 eV and therefore a better photocatalytic activity in the visible light spectrum. The isotherms obtained by nitrogen fisisorción are type IV which are characteristic of the mesoporous solids, in addition to presenting hysteresis loops of type 3 which agree with pores of parallel plates type, these results agree with the micrographs obtained in the MEB, in which the formation of bars and flakes characteristic of the synthesis method can be observed. Finally of the synthesized materials, the best was the Bi_2O_3:Gd 2%, which presented a crystalline structure in the tetragonal beta phase, which has been reported as the most photoactive phase.

4. Conclusions

The doping of Bi2O3 materials in different percentages could allow to improve their optical and structural properties, alpha and beta crystalline structure of the material was obtained, the beta phase showed the greatest photocatalytic activity, a transition between the crystalline phases was achieved by changing the percentage of gadolinium in $B_{i2}O_3$, materials with a Bandgap between 2.95 eV - 2.53 eV were also obtained, which allows a better photocatalytic activity of the material in the visible spectrum, the micrographs achieved the characteristic morphology of the synthesis method, finally the results obtained in Photocatalytic evaluation of hydrogen production showed that the

material with the best photocatalytic activity is Bi_2O_3: Gd 2%, probably due to the fact that it has the lowest Bandgap and a tetragonal beta crystalline structure, which has been reported as the most photoactive phase of Bi_2O_3.

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