Synthesis of GaN by hydrothermal method as promising photo-electrocatalyst for hydrogen production

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ABSTRACT

Gallium nitride (GaN) has been successfully synthesized using a hydrothermal method at 240 °C during 72 h. In order to increase the cristallinity grade, solid was calcined at 900°C under nitrogen atmosphere. X-Ray powder diffraction (XRD) confirms the characteristic reflection of wurtzite phase [050-079]. The images by Screening Electron Microscopy showed agglomerated particles in the range of 0.5 micrometre, however Transmission Electron Microscopy (TEM) reveals that particles are composed by hexagonal nanoparticles with a size below 20 nanometers. The measured interplanar distance confirms that microstructure corresponds to wurzite phase. From the point of view of superficial properties GaN has showed 64 $m^2.g^{-1}$, however after thermal treatment the specific surface area drop to 48 $m^2.g^{-1}$. IR analysis only showed important signals for metallic bond for underwaves below 1000 nm. These results promise interesting performance on hydrogen production by electrochemical and photogalvanic methods.

1. Introduction

The group III nitrides GaN, InN, InnGa1_nN, and AlnGa1_nN have recently acquired technological importance for blue/violet LED and laser diode applications [1] However, recently GaN has been shown like a material with very interesting characteristics for hydrogen production [2] and to achieve this application it becomes necessary to improve the synthesis routes to manipulate their physiochemical and optical properties with the purpose of developing sustainable technologies for energy generation[3,4].

Within emergent technologies for clean energy generation, the electrophotocatalysis plays a fundamental role, considering that main supplies (water and solar light) are resources that are available in the nature and that during the reaction they do not imply the generation of pollutants[5]. However, to promote this reaction it is necessary the use of semiconductors that allow the electrons located in the valency band to be

transported to the conduction band more efficiently. Thus promoting the water redox reactions by the action of light.

Although the first studies published on hydrogen production correspond to TiO_2[6], at the present time there are reported an important quantity of binary and ternary oxides with bandgap energy of up to 4.5eV[7,8]. On the other hand, the non-oxide type materials like the nitrides and the sulfides are more valuable by their low bandgap energy, which allows them to work from the near infrared up to UV [9].

Although, the conventional route of high temperature and NH_3 guarantee the formation of GaN [10]. The new technological requirements show a great interest in preparing GaN by routes of soft chemistry that guarantee the obtaining of nanostructured material to improve their properties at nanometric level [11,12]. In consequence, in this work the synthesis and characterization of synthesized GaN by hydrothermal method is presented.

2. Experimental Part

2.1 Synthesis

Gallium Nitride was prepared by hydrothermal route using Gallium Acetylacetonate (Aldrich, 99.99%) and Ammonium Acetate (Aldrich, 98%) as precursors with a stoichiometric relationship. As first step of preparation stage, in a three-neck flask a benzene solution (DEQ, 99.7%) with isopropanol (OmniSolv, 99.98%) in relationship 9:1 in volume was prepared, then Ammonium Acetate was added and the flask was placed on a grill with vigorous agitation and temperature of 50 °C. Next, pH was adjusted at 2 to assure the solution using HNO_3 (DEQ). Once complete solution of Ammonium Acetate was assured Gallium Acetylacetonate was added and agitation was continued until completing 24 h. When concluding agitation time the solution was placed in a PARR brand reactor and it underwent a thermal treatment at 240°C for 72 h. Then autoclave was cooled until ambient temperature and the synthesized material was recovered, which was washed three times with acetone for finally dry it at 100 °C for 12 h. With the intention of increasing the GaN crystallinity grade, the material was placed inside a quartz cell coupled to a tubular oven under a N_2 atmosphere and it was calcined at different temperatures (400, 600, 800, 850 y 900°C) for 15 h, to guarantee the formation of wurtzite phase.

2.2 Electrode preparation

Three milligrams of catalyst prepared as described in section 2.1, 3 µL of Nafion solution (Aldrich,5 wt%), 60 µL of ethanol (CTR, 99.95) and 30 µL of water were ultrasonicated for 30 min. 6 µL of this ink were deposited over an ITO film (8-12 Ω/sq) and dried for 40 min.

2.3 Characterization

The structural properties of samples were analyzed by X-Ray Diffraction in Rigaku MiniFelx II type equipment with Cu Kα (30 kV, 15 mA) radiation with a scan speed of 2°C.min^{-1}. Morphology of synthesized particles was observed by Scanning Electronic Microscopy (JEOL 6490LV) and by Transmission Electron Microscopy (JEOL, JEM-2010 F) with which was also carried out the chemical composition analysis (EDS). To observe transformations that exist in the material with regard to temperature there were carried out Thermal Gravimetric (TGA) and Thermal Differential (DTA) analyses in Perkin Elmer, Diamond TG/DTA equipment the interval from 25 to 1000°C using Nitrogen like carrier and an initial mass of 12.374 mg. The superficial and textural characterization of fresh materials was carried out in Auto-sorb 3B equipment using the technique of nitrogen physisorption. To support the results of structural and superficial characterization it was carried out GaN Infrared spectrometry (SIMADZU, IRAffinity 1). For the electrochemical characterization, a three-electrode standard cell was employed. A carbon rod and a Calomel (SCE) electrode were used as counter and reference electrodes, respectively. Prior to use, the solution was purged with argon for at least 15 min. The i-E characteristics were recorded in the interval from 0.0V to -1.0V/SCE using linear sweep voltammetry at scan rate of 5mV/s. Solution 0.1 M of H2SO4 was used as supporting electrolyte. The electrochemical experiments were done with a Potentiostat/Galvanostat (VersaStudio). For photogalvanic experiments, two-containers (half-cells), separated by a salt bridge, were used. The anode half-cell consisted of the photoanode ITO or ITO modified with GaN in a KBr solution. The cathodic half-cell consisted of an H_2SO_4 solution and platinum sheet as electrode. The photoanode in turn was illuminated with UV light during 35min and the current signal was monitored as a function of time.

3. Results and Discussions

3.1 X-Ray Diffraction

In Figure 1 the results of X-Ray Diffraction of Gallium Nitride synthesized by hydrothermal route and the material calcined at different temperatures are shown. In accordance with Curve A it is observed that fresh

material has wide peaks and although they are not totally defined the reflections at 2θ=36.85 is characteristic of GaN [IJPCD No. 050-0792] main peak. In accordance with that reported by Yi Yang and collaborators [13] it is possible the obtaining of GaN by the inorganic route using like base in xerogels. Starting from their X-Rays results, they assure to obtain GaN, however it is evident that their material is totally amorphous compared with our synthesis at 240°C.

In curves B, C, and D the thermal evolution of GaN is shown, but up to 800 °C (curve E) the reflections of XRD analysis show a better definition of GaN although even has some characteristic signs of β-Ga_2O_3. However, when GaN calcined at 900°C, the characteristic reflections of Gallium Nitride totally prevail and they coincide with signs reported in card IJPCD No. 050-0792 and whose Miller indexes are shown in Figure 1 which are typical of wurtzite phase with hexagonal geometry. This result coincides with that reported by H.D. Xiao and collaborators [14] who obtained GaN by route of solid state at same temperature, with the inconvenience that they even obtain some peaks characteristic of Ga_2O_3.

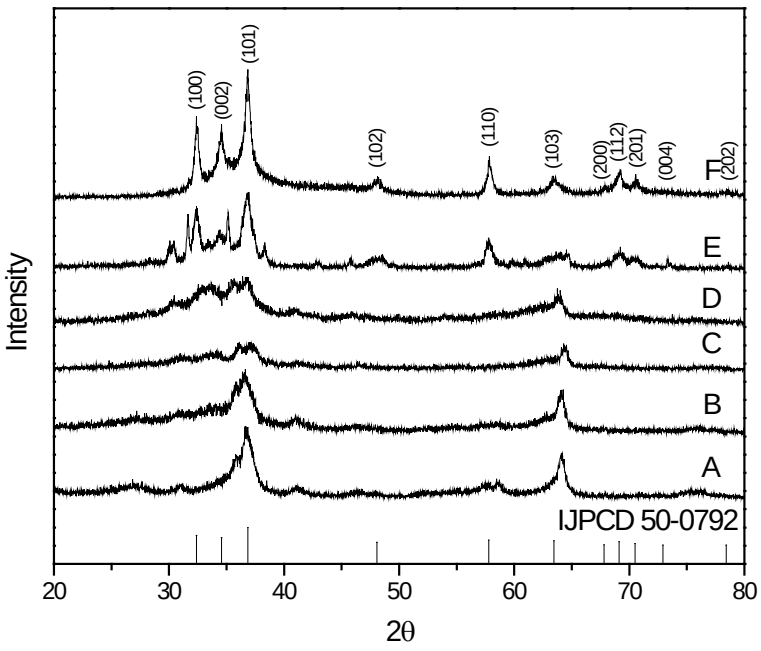

Figure 1. X-Ray Diffraction patterns corresponding to GaN synthesized by hydrothermal route at 240°C/72 h at different thermal treatments for 15 hours. A) 240 °C, B) 400 °C, C) 600 °C, D) 800 °C, E) 850 °C and F) 900 °C.

3.2 Thermogravimetric analysis

With the purpose of identifying in the material the transformations that occur in function of temperature the thermal analyses for material synthesized by hydrothermal route were carried out. In accordance with results shown in Figure 2, it is observed that thermo-differential analysis presents an entothermal peak in the interval from 340 to 510 °C and that it is attributed to elimination of materials mainly compound by Carbon and Nitrogen according to that reported for other systems synthesized starting from organic precursors [15]. At temperatures greater than 650 °C, the material presents thermal stability, however around 850 °C a slight exothermal peak is presented that can possibly assign to GaN crystallization, in this case, to formation of wurtzite phase. This result coincides with that mentioned in the XRD analyses.

By means of thermal-gravimetric analysis it was obtained accordance with previously mentioned, that is to say, the curve B presents a weight loss of 11.3% in the low temperature area (310 to 620 °C) and then a slight interference of line base for wurtzite formation.

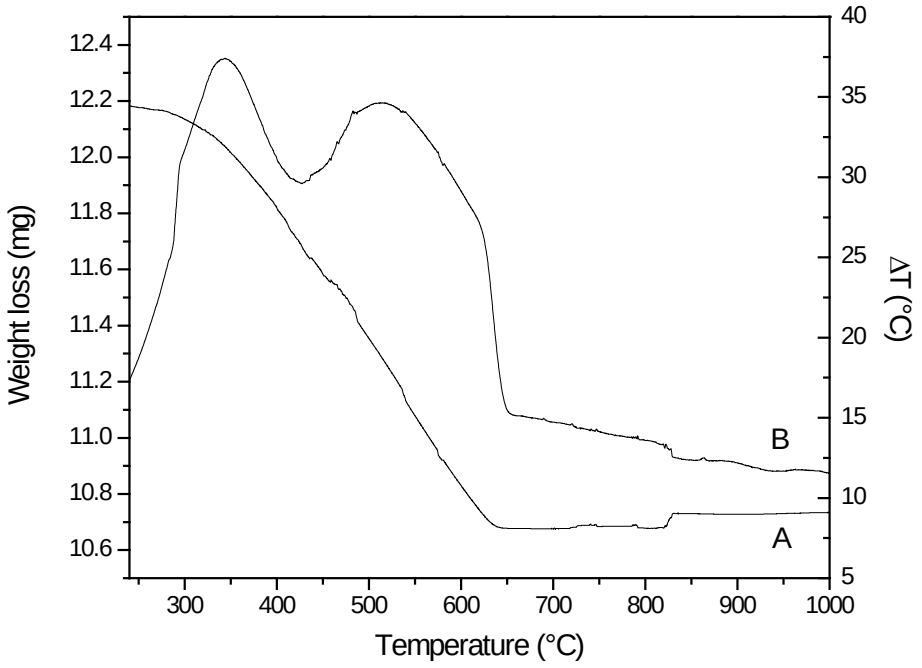

Figure 2. Thermal analysis of GaN synthesized by hydrothermal route at 240 °C during 72 hours. A) Weight loss (mg), B) Differential of temperature (°C).

3.3 Scanning Electron Microscopy.

In Figure 3 the GaN micrographs are presented synthesized by hydrothermal route calcined at 900 °C for 15 h. In the image 3A a heterogeneous material is observed with particles of around 0.2 mμ which form bigger agglomerates. Image 3B shows in detail the trend to form agglomerates through synthesis route. In certain regions of micrograph indicated with arrows the presence of semi-spherical morphologies is evidenced with a size distribution so much uniform and with tend of forming agglomerates. This result coincides with that reported by Sungryong Cho and collaborators [14] who show a size distribution average 0.1 μm in a prepared material for route of solid state using ammonia like nitrogen precursor and obtaining morphologies similar to flakes. [14,16].

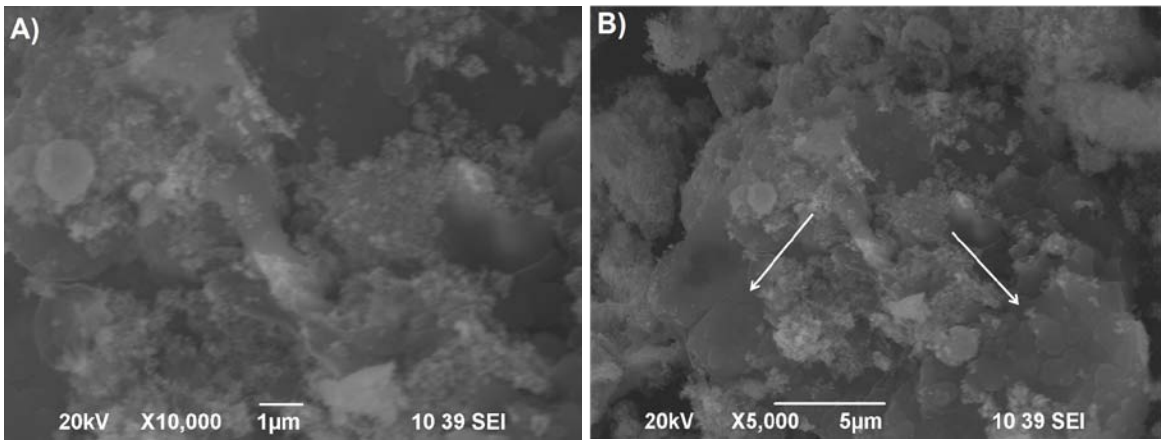

Figure 3. SEM micrographs of the material calcined at 900 °C / 15 h. A) 1μm, B) 5μm.

3.4 Transmission Electron Microscopy.

With the purpose of confirming GaN nanoparticles obtention by hydrothermal route, the analysis of transmission electron microscopy was carried out. In Figure 4A images of GaN particles are shown highlighting that sample contains crystals agglomerated with great disorder and whose sizes between 10 and 22 nm according to histogram that is shown giving an average size of 17 nm (Figure 4B). This tend coincides with that published by M. Nyk and collaborators [17]. Since the synthesis conditions in the hydrothermal route are not aggressive, perhaps this allows the obtaining of small particles compared with the particles of GaN synthesized by solid state reported by B. C. di Lello [18] which are average particles of 40 nm. When calculating the interplane distance of the planes that appear of HRTEM micrograph was determined that they correspond to the plane (002) with a distance of 0.26 nm as them are showed in images 4C and 4D [19,20].

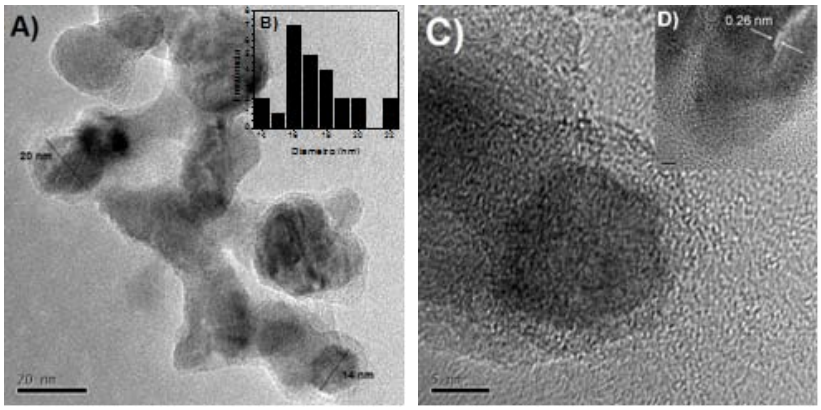

Figure 4. HRTEM Micrographs of GaN synthetized by hydrothermal method and calcined at 900 °C / 15 h. A) 20 nm scale, B) Histogram (insert), C) 5 nm scale, D) Interplane distance.

3.5 BET superficial area

During design of new materials it is important to know the structural and superficial properties. In this work it was carried out the nitrogen physisorption analysis to know GaN superficial area by hydrothermal route (240 °C) and calcined (900°C). In accordance with the results for the material at 240 °C an area of 64 $m^2.g^{-1}$ was obtained, while superficial area of calcined material diminished 48 $m^2.g^{-1}$. This decrease of 25% in the area is not significant taking in consideration the gradient of temperature at which sample was subjected to. Up to now, in the literature this property is not reported, very possibly because the GaN applications are directed toward synthesis of films for applications in solar cells and LED's. [21-23].

3.6 Infrared spectroscopy.

To reaffirm results obtained by XRD, samples were analyzed by Infrared Spectroscopy. In the curve A of figure 5 are shown two characteristic bands to Ga-N bond near to 605 and 555 cm^{-1} [20], although we can also find N-H and C-O bond near to 1586 y 767 cm^{-1}. The curve B is presented in the near values to 908 y 639 cm^{-1} corresponding to O-H bond and those characteristic of Ga-N bond in 580 and 550 cm^{-1} [25-26].

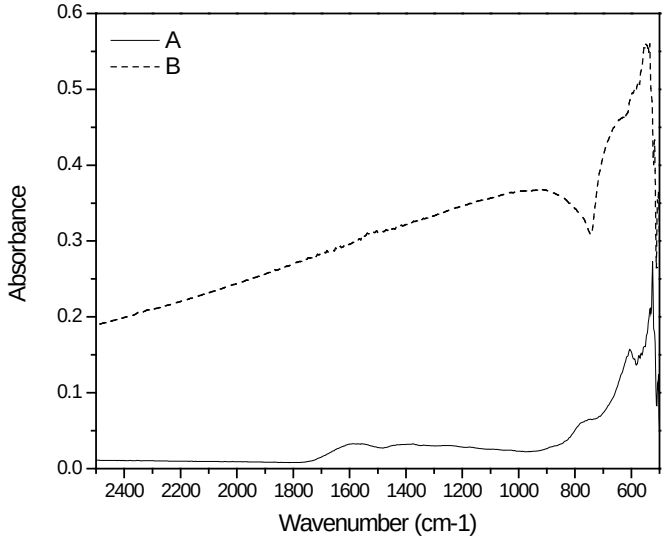

Figure 5. Infrared spectroscopy. A) GaN synthesized by hydrothermal route at 240 °C, B) GaN calcined at 900 °C.

3.7 Linear-sweep Voltametry (LSV)

Linear polarization profiles of GaN (curve B) and ITO (curve A), in a solution of 0.1M H_2SO_4 and at scan rate of 5mV/s, are depicted in Figure 6. The production of hydrogen started at -0.4V/SCE for ITO. Conversely, the HER kinetic is faster for GaN. In this last material, the hydrogen production begins at ca. -0.3V/SCE with an important difference in the faradaic current with respect to the substrate (i.e. ITO). Therefore, at the conditions described here, the overpotential for HER is less intense at GaN modified electrode as the proton adsorption-desorption kinetic is more effective, linked to its intrinsic properties given for the preparation route. These preliminary results confirmed that the synthesized semiconductor might be an important alternative for the production of hydrogen, see below.

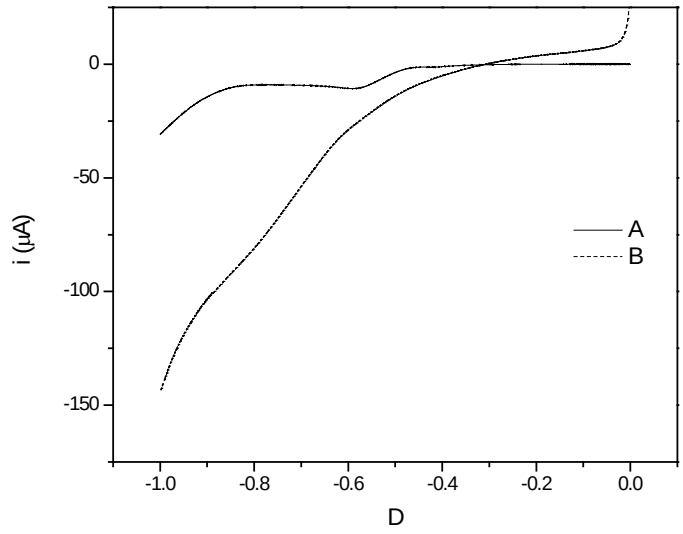

Figure 6. i-E characteristic for A) ITO, B) GaN at 900 °C. Scan rate of 5 mVs^{-1}

3.8 Photo-galvanic experiments

In order to give further confidence concerning the hydrogen production as has been observed in the i-E characteristics of Figure 6, photogalvanic experiments were carried out as described in the experimental section. The obtained profiles i-t are shown in Figure 7 for ITO (curve a) and GaN-ITO (curve b). Notice that the photocurrent magnitude corresponding to the modified ITO with GaN is more intense. A deeper analysis of these profiles put in evidence that the current magnitude decreases as a result of the progressive depletion of electroactive species at the electrode surface, associated to ion exchange from bulk solution. Then, the light-induced charge separation by photoexcitation of electrons from the valence band to the conduction band, permit the formation of electron–hole pairs in the semiconductor bulk. In this context, the diffusion of photoexcited electrons and holes in opposite directions generates the photo-induced current profiles observed in Figure 7. In this particular system, the spatial separation of the electric charges is achieved by an electron donating species (Br^- ions) in the vicinity of the electrode interface in order to compensate the electron deficit. Also, open circuit potential (OCP) transient profiles (Figure not shown) demonstrated that the potential is more negative for the as-prepared material.

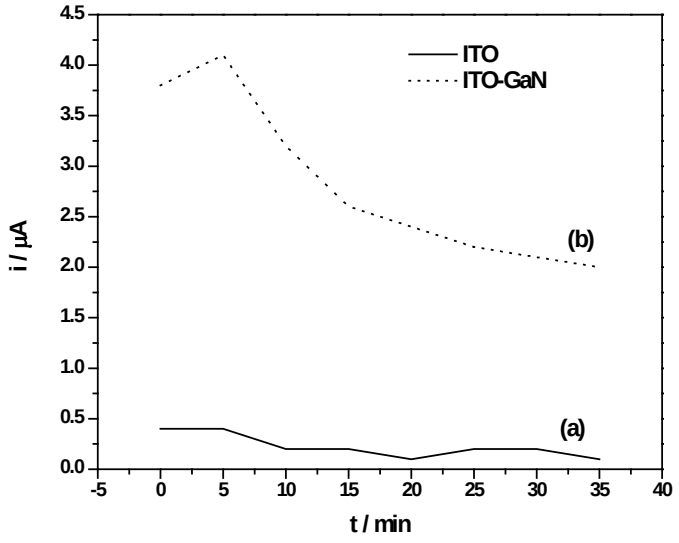

Figure 7. i-t transients for the ITO substrate (a) and ITO modified with GaN (b) obtained by photogalvanic experiments.

4. **Conclusions**

Gallium nitrate was synthetized by hydrothermal method at 240 °C. The physicochemical characterization by XRD confirms the formation of crystalline GaN at 900°C with wurzite phase. The HRTEM analysis shown highlighting that sample contains crystals agglomerated with great disorder and whose sizes are between 10 and 22 nm. When calculating the interplane distance of the GaN planes it was determined that there correspondence to the plane (002) with a distance of 0.26 nm according with the XRD analysis. The nitrogen physisorption analysis reveals a low loss of the surface area by effect of thermal treatment, which result interesting for photo-electrocatalytic applications. The electrocatalytic activitiy of GaN was evaluated using LSV. Preliminary results indicated that the proton adsorption-desorption kinetic is more efficient in the home-made semiconductor. As a consequence, the generated photocurrent at the interface of GaN is more important compared with the substrate employed.

5. **Aknowledgments**

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