# KNbO$_3$ as Photocatalyst for Hydrogen Production

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## ABSTRACT

Semiconductor photocatalytic water splitting to produce hydrogen from solar energy has been considered as one of the most important approaches in achieving an energy based sustainable development. A large number of semiconductor materials have been proposed as photocatalysts for water splitting to hydrogen. The pervoskite-structure compounds have attracted wide attention over the past half a century. MNbO$_3$ (M = Li, Na or K) is a pervoskite oxide with unique physical and chemical properties such as low density, high sound velocity, photorefractive effect and photoactivity. These materials have presented remarkable photocatalytic activity for water splitting and environmental purification. Moreover, potassium niobate (KNbO$_3$) submicro-crystals were prepared by a soft chemical method and characterized by powder X-ray diffraction, nitrogen adsorption–desorption, diffuse reflectance UV–visible spectroscopy, and scanning electron microscopy. The photocatalytic performance was evaluated toward H$_2$ generation from an aqueous methanol solution (2%Vol) under UV and Vis light using a 250 W mercurial lamp as an irradiation source. XRD results found that synthesized KNbO$_3$ presented an orthorhombic rhombohedral phase. Crystallite size was estimated using the XRD data and the Debye-Scherrer equation, reaching ~ 43.4 nm. From UV–visible spectroscopy it was found that KNbO$_3$ exhibited a band gap energy of 2.98 eV. The BET surface area of the synthesized sample was 1.80 m$^2$/g. Photocatalytic activity of potassium niobate presented a hydrogen production of 350 µmol/g $_{catalyst}$ using a reactor loading of 200 mg of photocatalyst under a 5 h irradiation time. Results from this study indicate that KNbO$_3$ perovskite is potentially applicable for the production of H$_2$ through photocatalytic water splitting.

*Keywords:* KNbO$_3$, Hydrogen production, Photocatalysis.

## 1. Introduction

The lack of energy resources and increasing pollution associated with energy production by conventional pathways, stimulated the search for cleaner, cheaper and more efficient energy technologies [1]. In recent years the production of hydrogen has received much attention due to its potential application as a clean energy source. Hydrogen can be obtained from renewable resources and produces only water vapor during combustion [2, 3].

Currently, hydrogen is mainly produced by reforming of oil and natural gas at high temperatures [4-7]. The photocatalytic splitting of the water molecule is a promising technology to produce "clean" hydrogen and this process is inexpensive compared to thermochemical or photobiological process [8]. The perovskite structure ($ABO_3$ where A is a metal, B is a second metal and O is oxygen) is one of the most studied structures among photocatalysts, due to their good photocatalytic as well as physicochemical properties [9-13].

Various compounds photocatalytic such as niobates, tantalates and titanates, have been reported towards the production of hydrogen by the dissociation of the water molecule with reasonable activity [14, 15]. The main objective of this study is to evaluate the photocatalytic activity of commercial and synthesized potassium niobate (KN) samples from three different synthesis methods. The study took place through: (1) the synthesis of KN nanoparticles using three synthesis methodologies; (2) the characterization of the commercial and KN synthesized powders and the; (3) the evaluation of photocatalytic activities of all KN samples.

## 2. Experimental

### 2.1. Catalysts Synthesis

$KNbO_3$ nanoparticles were prepared a by soft chemical method, using stoichiometric amounts of $C_4H_4NNbO_9 \cdot xH_2O$ (Aldrich) and $KNO_3$ (Fermont). Three different synthesis methods were used to prepare powders KN, these methodologies are generally shown in Figures 1 to 3. Furthermore, Table 1 presents the nomenclature used to identify the KN samples studied.

Table 1. Identification KN samples.

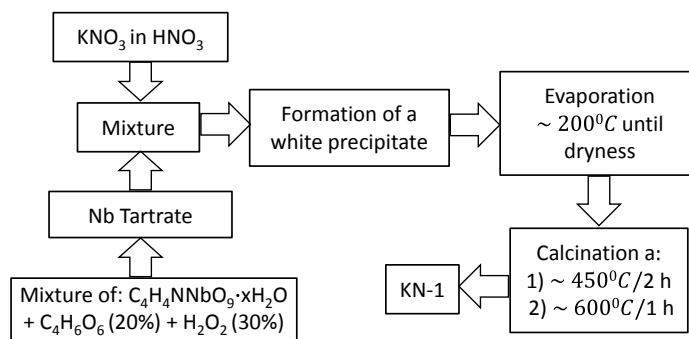| Nomenclature | Synthesis Method |
|---|---|
| KN-c | Commercial sample (Alfa Aesar) |
| KN-1 | Based on the methodology used by Bhattacharyya and Tyagi 2009 [16] |
| KN-2 | Based on the precipitation method employed by Cabrera Lopez et al. 2009 [17] |
| KN-3 | Based on the combination of the methods used to synthesize KN-1 and KN -2. |

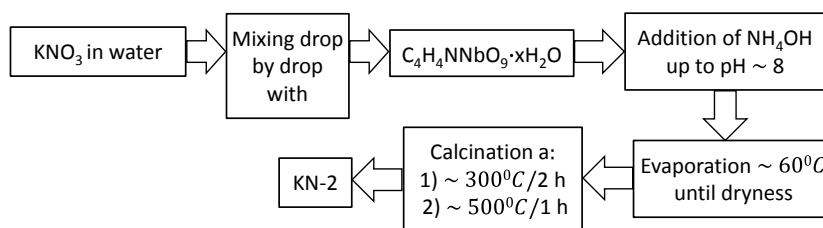Fig 1. General methodology for the synthesis of KN-1 nanoparticles.

$KNO_3$ in $HNO_3$

Mixture → Formation of a white precipitate → Evaporation $\sim 200^0C$ until dryness

Nb Tartrate

Mixture of: $C_4H_4NNbO_9 \cdot xH_2O$ + $C_4H_6O_6$ (20%) + $H_2O_2$ (30%)

KN-1 ← Calcination a: 1) $\sim 450^0C/2$ h 2) $\sim 600^0C/1$ h



Fig 2. General methodology for the synthesis of KN-2 nanoparticles

$KNO_3$ in water → Mixing drop by drop with → $C_4H_4NNbO_9 \cdot xH_2O$ → Addition of $NH_4OH$ up to pH $\sim 8$

KN-2 ← Calcination a: 1) $\sim 300^0C/2$ h 2) $\sim 500^0C/1$ h ← Evaporation $\sim 60^0C$ until dryness
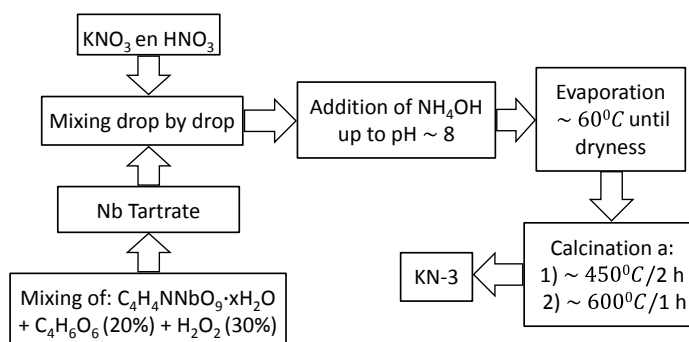


Fig 3. General methodology for the synthesis of KN-3 nanoparticles

$KNO_3$ en $HNO_3$

Mixing drop by drop → Addition of $NH_4OH$ up to pH $\sim 8$ → Evaporation $\sim 60^0C$ until dryness

Nb Tartrate

Mixing of: $C_4H_4NNbO_9 \cdot xH_2O$ + $C_4H_6O_6$ (20%) + $H_2O_2$ (30%)

KN-3 ← Calcination a: 1) $\sim 450^0C/2$ h 2) $\sim 600^0C/1$ h

The general synthesis methodology of Figure 3 is based on the combination of the methodologies employed for KN-1 [16] and KN-2 [17]. Based on this, the mixed solutions of $KNO_3$ and tartrate aqueous solution at basic pH were used; besides controlling the addition of nitrate at 0.5 mL/min in aqueous tartaric solution.

### 2.2. Catalysts Characterization

The phase composition and crystallinity of the sample powders were analyzed by X-ray diffraction in a Panalytical brand, model X'Pert PRO diffractometer with CuKα radiation. Samples morphology were evaluated by field emission scanning electron microscopy in a SEM, JSM-7401F. The bandgap energy of the sample powders were obtained by the UV-Vis diffuse reflectance spectrum using a UV-Vis

spectrometer (Lambda 10, Perkin Elmer) equipped with integrating sphere (Labsphere RSA-PE-20). The specific surface area was determined using the Brunauer-Emmett and Teller (BET) method (Micromeretics Atosorb). The characterization was performed on the synthesized samples: KN-1, KN-2 and KN-3 and commercial: KN-c (see Table 1).

### 2.3. Catalysts Activity Evaluation

0.2 g of each KN Photocatalyst was evaluated by splitting of the water molecule, using a 250W mercurial lamp and adding methanol to the water reactor system as sacrificial agent (2% vol). The reaction was monitored by gas chromatography using a GC Perkin Elmer Clarus 500. The system setup employed for carrying out the photocatalytic evaluation of the materials is composed by a photoreactor, artificial lighting and GC analysis with a PC data collection. In order to monitor the photocatalytic reaction, samples were taken at regular time intervals using a 1ml syringe for gases through a septum located at the upper section of the photoreactor. A sample under darkness was taken as the initial concentration and then the sampling was took place every hour up to a total of 10 hours of irradiation.

## 3. Results and discussion

### 3.1. X-Ray Diffraction

Figure 2 presents XRD diffractograms of the four catalysts in study. Form this Figure it can be seen that the only crystalline phase present in all samples is that one corresponding to the pure $KNbO_3$ phase. With the X-ray patterns information and applying Scherrer's equation the crystallite size of the powders was calculated. The crystallite size of synthesized catalyst was smaller than the commercial catalyst, with values of: 39.3 nm, 48.6 nm, 43.4 nm and 91.7 nm corresponding to KN-1, KN-2, KN-3 and KN-c, respectively.
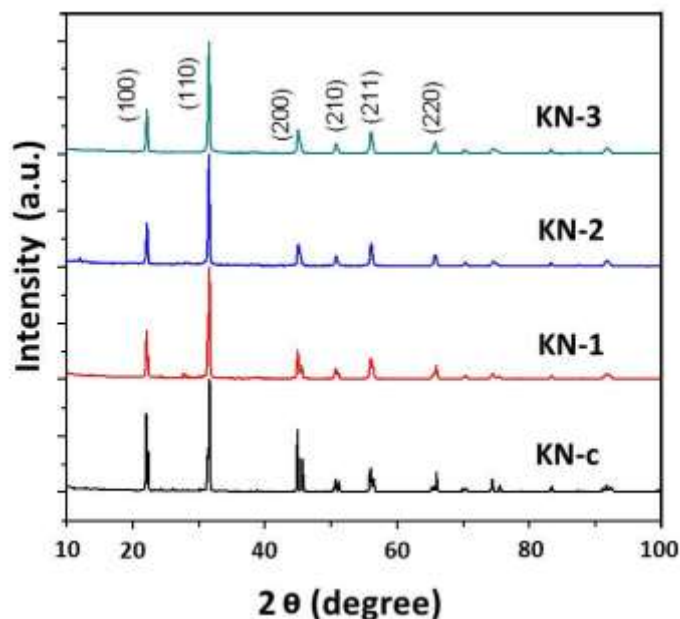


Fig 2. XRD diffractograms of the commercial and synthesized KN powders.

Furthermore, XRD diffractograms of the different synthesized KN samples presented in Figure 2 are similar to those obtained by some other authors such as Shi et al. 2012, Liu et al. 2007, Kinoshita et al. 2012 and Wang et al. 2013 [18-21].

*3.2. Morphology and specific surface area*

During the sample preparation for SEM analysis, the catalysts particles were previously dissolved in isopropanol and dispersed using an ultrasound machine. Subsequently the catalysts were deposited onto a silica sample holder.
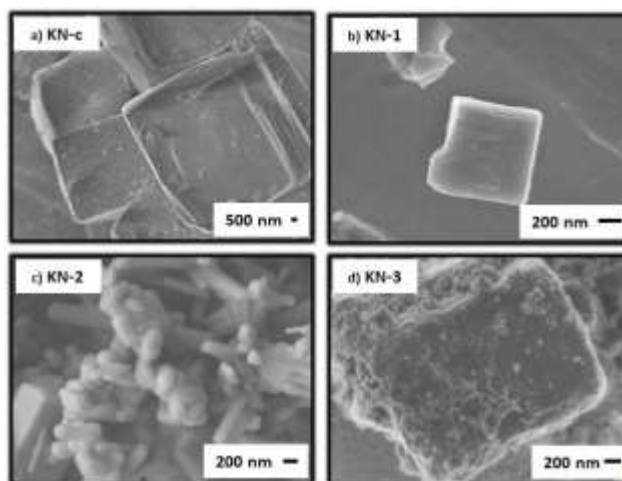


Fig 3. SEM images of the of commercial and synthesized KN catalysts.

Figure 3 shows SEM images of commercial and synthesized KN catalysts. From this Figure It can be seen that the catalysts present a similar morphology, except for sample KN-2 (see Figure 3c) with tubular shape and particles with a diameter of approximately 200 nm. Moreover, the KN-1 and KN-c catalyst (see Figure 3a and 3b) exhibit a particle diameter of 600 nm and 8 µm, respectively. However, catalyst KN-3 (see Figure 3d) involves clusters of small particles with approximate 150 nm, while this is the catalyst having the smallest particle size, compared to the other studied catalysts. The difference in particle size KN synthesized catalysts, can be attributed to the employed synthesis methodology.

Liu et al. 2007 [20] synthesized KN by hydrothermal synthesis and obtained a particle size in the range of 100 to 150 nm, similar to the one obtained in this study for KN-3 (without the presence of agglomerates). In another study Kinoshita et al. 2012 [21] conducted KN synthesis by the solid state technique and similar morphologies to KN-3 were obtained (see Figure 3d), however larger particle sizes (~20 um) for KN samples were produced in this study. Furthermore, using a hydrothermal synthesis of KN Yan et al. 2007 [4] reported similar size and morphology to those obtained in KN-1 sample.

Moreover, the average values of the BET surface area obtained for KN-c, KN-1, KN-2 and KN-3 were 0.47, 0.5, 4.6 and 1.8 $m^2g^{-1}$, respectively.

### 3.3. UV-Vis Spectroscopy

The optical properties of the KN nanoparticles were measured through the UV/Vis diffuse reflectance absorption spectrum and these are shown in Figure 4.
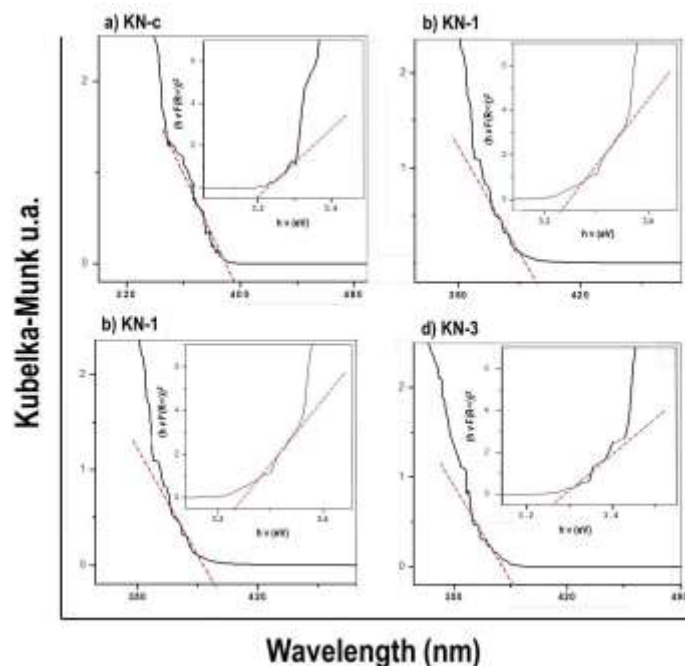


Fig 4. UV-Vis diffuse reflectance spectra and determination of the band gap energy for the different commercial and synthesized KN samples.

UV/Vis diffuse reflectance spectra for the KN powders were converted in terms of absorption using (F (R)) function of Kubelka-Munk to determine in which region of the visible light the material is located; and the forbidden band width. Niobates powders show strong absorption in the visible light region and the optical absorption peaks were very similar to each other (see Figures 4a to 4d), while these were located around 400 nm. Furthermore, the KN bandgap energy was found around 3.2 eV (see Figure 4), with spectra similar to each other (see Figures 4a to 4d). The small differences among the values obtained from KN powders, may be due to the difference in crystallite sizes.

### 3.4. Photocatalytic Activity

The photocatalytic activity of the commercial and synthesized KN nanoparticles were evaluated through the gas hydrogen production. Figure 5 shows the performance of the photocatalytic activity of the KN catalysts during an irradiation time of 6 h.
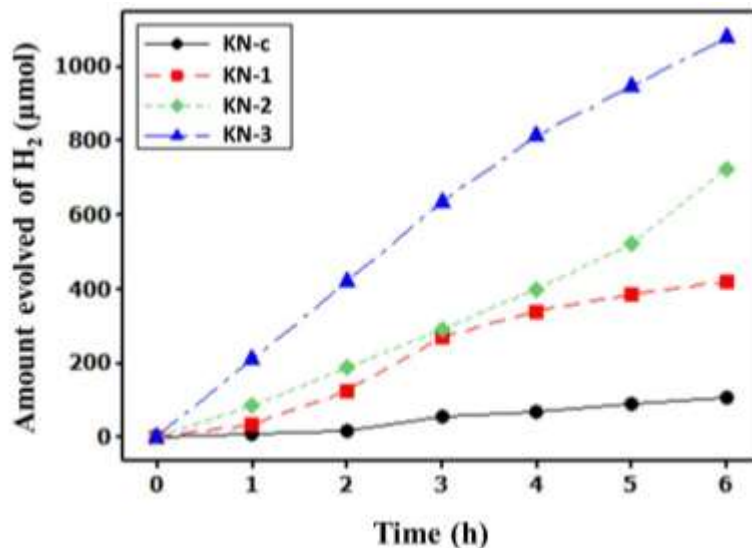
Fig 5. Photocatalytic $H_2$ production under conditions of visible light irradiation for KN samples.

Table 2 shows a summary of the KN powders photocatalytic activity results carried out under study. The results obtained in a period of 6 h of irradiation (Table 2) show that KN-3 presents a remarkable deference in $H_2$ production over other synthesized powders in a magnitude of 11 times more than the KN-c powder.

Table 2. Results Summary for the characterization and photocatalytic activity of the KN catalysts.

| Catalyst | Surface Area (m$^2$ g$^{-1}$) | Band Gap (eV) | Crystal (nm) | UV-Vis (nm) | Photocatalytic Activity * (µmol) |
|---|---|---|---|---|---|
| KN-c | 0.47 | 3.19 | 91.7 | 396 | 106.54 |
| KN-1 | 0.50 | 3.23 | 39.3 | 427 | 421.70 |
| KN-2 | 1.13 | 3.27 | 48.6 | 412 | 727.32 |
| KN-3 | 1.80 | 3.26 | 43.4 | 409 | 1081.14 |

**\*** Photocatalytic activity obtained at 6 h of irradiation and using 0.2 g of photocatalyst.

The value of the band gap energy for different KN samples in this investigation was found to be similar to those reported by Ding et al. 2008, Yan et al. 2013 and Liu et al. 2007 [4, 10, 20]. Also, in order to make a comparison of the $H_2$ production from this study with other studies in terms of the KN photocatalytic activity, it was found that: Liu et al. 2007 [20] obtained a lower $H_2$ production compared to the production obtained by using the synthesized catalysts in the present research (see Table 2); Ding et al. 2009 [10] reported twice the $H_2$ produced as compared to KN-3, but using a two-lamp irradiation intensity than that used in this study and 14 times the same sacrificial agent and Yan et al. 2013 [4] obtained a similar production of $H_2$, although using Pt as co-catalyst.

## 4. Summary and perspectives

KN nanometric powders were obtained using different synthesis methods, which showed values of bandgap energies within the spectrum of visible light and showed photocatalytic properties for the dissociation of the water molecule. The KN-3 synthesized material showed the highest hydrogen production, compared to the KN-c (commercial) and synthesized KN-1 and KN-2 samples. Based on the results obtained in this study the photocatalytic decomposition of water may be a promising alternative for the production of hydrogen using as niobates materials as water splitting photocatalysts.

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