Chapter 1.13. Synthesis, characterization and photocatalytic evaluation of MWO_4 (M = Ni, Co, Cu and Mn) Tungstates

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ABSTRACT

Photocatalysis is an technology that can be applied to solve environmental and energy problems such as the production of hydrogen from the dissociation of the water molecule. Tungstates exhibit many potential applications in different areas of technology due their excellent electrical properties. Nanostructured tungstate materials are known for their wide applications in conventional catalysis, as scintillator material, in photoluminescence, optical fibres and as materials in microwave technology. Eventhough these present enough chemical and thermal stability, very scarce reports are found in the literature related to their uses as photocatalysts for hydrogen production through water splitting. The aim of the present study is the synthesis and characterization of family tungstate MWO_4 (M = Co, Cu, Mn and Ni) materials through co-precipitation in order to evaluate their photocatalytic activity towards the production of hydrogen within the visible light range. Characterization consisted in XRD, BET, UV-Vis and SEM, while the photocatalytic evaluation was as follows: 200 mg of $CuWO_4$, $CoWO_4$, $NiWO_4$ and $MnWO_4$ powders were individually suspended in water and methanol, the latter used as a sacrificial agent. The water suspension was placed inside a sealed quartz batch photoreactor under constant stirring and and illuminated by a 250W mercury lamp for 8 h with gas evoultion being monitored by gas chromatography (GC). Preeliminary results indicate that the employed synthesis method was effective to obtain the required crystalline phase. However, optimal conditions are needed to decrease particle size and increase the tungstates surface areas. The bandgap energy of these tungstates was found to be within the visible light spectrum with a variation between 2.24 eV for $CoWO_4$ to 2.56 eV for $MnWO_4$, respetively. Maximum hydrogen production was achieved by sample $MnWO_4$ with 139 $\mu mH_2/g_{cat}$, while the lowest production was observed for sample $CoWO_4$ with 24 $\mu mH_2/g_{cat}$. From these preeliminary results it can be infered that simple and mixed metal transition tungstates can be considerer as potential candidates, as photocatalysts for H_2 production via the splitting of the water molecule under visible light irradiation.

Keywords: H_2 generation; water splitting; photocatalysis; tungstates

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1. Introduction

Catalysis is called to the change in reaction rate due to a participation of an agent called catalyst. This catalyst not only makes possible the chemical reaction to occur in a faster rate, but also lowers the activation its energy, while not being part as a reactant or product. When the catalytic reaction is activated through light absorption it is called phtotocatalysis, [1] and this is defined as a chemical reaction induced by photo iradiation in the presence of a photocatalyst [2]. Such a material facilitates chemical reactions whitout being consumed or transformed. This process starts when a semiconductor material is iluminated with a suitable wavelenght of light that must be equal or higher to the size of the band gap energy of a semiconductor. The general idea of using a fotocatalyst to split the molecule of water consists in use the oxydizing and reducing effect of the charges that are generated in a semiconductor [1]. Photocalysis can be applied to solve enviromental and energy problems [3-5], such as hydrogen production from water splitting. Some of the advantages of the photocatalysys are: low processing costs, the capability of hydrogen and oxygen evolution during the water splitting reaction and suitable small reactor systems for domestic applications, thus providing a huge potential market [2].

Scheelite and wolframite type compounds such as tungstates (AWO_4) are part of an important family of materials from a technogical point of view. According to the literature, Rajagopal et. [6] tungstates present different and interesting properties, that draw attention, because they exhibit potential applications in different technological areas [7], such as; state solid laser [8], microwave, scintillation [9], optoelectronic devices, optic fibers [6], humidity sensors and fluorescent lamps due to their photoluminicense appeling properties, meanwhile some others tungstates are of special interest due to their conductivity and electrical properties [10]. According to the above, these materials could be considered as potential photocatalysts towards the hydrogen production.

Moreover, the coprecipitation synthesis route is a simple, fast and a soft chemical method. Furthermore, it has many advantages such as; low calcination temperature, low cost ,and above all it does not require special operating conditions [11]. This technique is probably the most used to prepare ceramic powders [12]. Garcia-Perez et al. [13] carried out the synthesis of bivalent transition metal tungstates such as; Co^{2+}, Cu^{2+}, Mn^{2+} and Ni^{2+} prepared through coprecipitation, where $CuWO_4$ series presented the greatest photocathalytic activity. Therefore, the objective of the present work is the synthesys, characterization and photocatalytic evaluation of materials of the tungstate family MWO_4 (M=Cu, Co, Ni and Mn) through the water splitting reaction towards the hydrogen production under the visible light irradiation.

2. Experimental

2.1. Synthesis of precursor solutions

The synthesis of MWO_4 compounds was caried out by the reaction in solution method. This technique consists in a disolution-precipitation reaction of salts containing the metals of interest; this method may lead, sometimes, to amorphus materials that through an adequate thermal treatment, can be transformed into crystalline materials with an optimal

morphology and microstructure.

Initially, the equivalent amount of 0.4 moles of $Na_2WO_4 \cdot 2H_2O$ were weighed in grams and dissolved in 1000 mL of distilled water (solution A). Then, four 0.4 M solutions of divalent cations (0.4 mol/1000 mL in distilled water) were prepared separately, using as reactants their hydrated nitrates: $Mn(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (solution B). Next, solution A was slowly added to solution B at room temperature and under vigorous stirring. The general chemical reaction that dictates the dissolution-precipitation method is the following:

$$M(NO_3)_2 + Na_2WO_4 \rightarrow MWO_4\,(\downarrow) + 2\,NaNO_3\,(M = Co^{2+}, Cu^{2+}, Mn^{2+}\ y\ Ni^{2}) \quad (1)$$

When mixing of both solutions in a 1:1 molar ratio took place, a precipitate was spontaneously formed. This was washed four times with DI water and filtered, whereas pH of the solutions was not adjusted. The obtained precipitates were dried at 100°C for 24h, grounded in an agate mortar, and finally calcined at 400°C during 4h. Sample nomenclature was set as follows: (a) $CoWO_4$, (b) $MnWO_4$, (c) $NiWO_4$ and (c) $CuWO_4$.

2.2. Characterization of materials

The MWO_4 (Co^{2+}, Cu^{2+}, Mn^{2+} y Ni^{2+}) powders were characterized using in X-ray diffraction (XRD), Breunner-Emmet-Teller Surface area (BET), diffuse reflectance spectroscopy (UV-Vis) and scanning electron microscopy (SEM) techniques to study their physical and chemical properties.

The synthesized powders were analyzed to determine their crystalline structure, through the X-ray diffraction technique, using a D8 Advance Bruker Axs diffractometer with Cu-Kα (λ = 1.5418 Å) radiation, scintillation detector and a Ni filter. Measurements were performed in a 2θ interval from 10 to 80° and using a step size of 0.016°/sec in an acrylic sample holder. The powders surface area was studied by the nitrogen physisorption technique at a degasification temperature of 180°C, using a Quantachrome Autosorb-1. For the measurement of the bandgap energy a UV-Vis Perkin Elmer (Lambda-10) spectrophotometer equipped with an integration sphere for the diffuse reflectance studies was used. While morphological characterization of the synthetized materials was carried out by scanning electron microscope technique using a SU 3500 HITACHI equipment. While, samples were chemically analyzed by dispersive spectroscopy (EDS) and chemical mapping using secondary electrons (SE) at 2 kX.

2.3. Photocatalytic evaluation

Photocatalytic evaluation of the synthesized samples towards the hydrogen production by water splitting was performed using a 250W mercurial lamp and 0.2 g of tungstate sample suspended in 200 mL of DI water and 4 mL of methanol in the reactor system as sacrificial agent (2% vol). The suspension was placed inside quartz photo reactor with a length and diameter of 19 and 5 cm, respectively, then it was hermetically sealed and placed 7cm away from the 250W mercury lamp. The photoreactor was kept under constant stirring and irradiated for 8h [14]. The reaction was monitored by gas chromatography using a gas chromatograph (GC) Perkin Elmer Clarus 500. The experimental setup employed for carrying out the photocatalytic evaluation of the materials is presented in Figure 1. This setup is composed by a photoreactor, artificial lighting, and GC analysis

equipped with a personal computer data collection. In order to monitor the photocatalytic reaction, gas 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 at the initial concentration and then the sampling took place every hour up to a total of 8 hours of continuous irradiation.

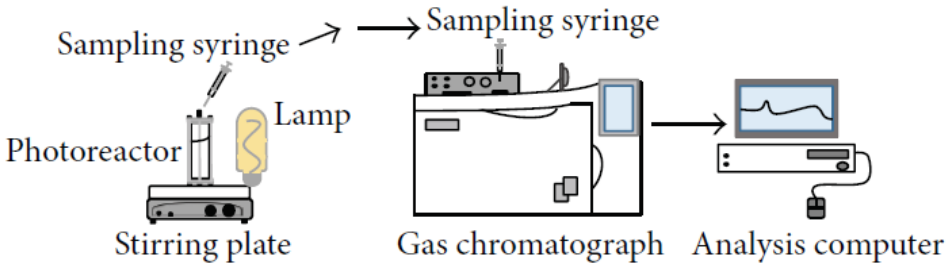

Fig. 1. Experimental setup for the photocatalytic evaluation of the tungstate samples.

3. Results and discussion

3.1. X-ray diffraction tests

Bivalence metal tungstate powders derived from the synthesis by the dissolution-precipitation technique were structurally characterized using XRD. Figure 2 shows the difractogram peaks of the synthetized photocatalysts (Co^{2+}, Cu^{2+}, Mn^{2+} and Ni^{2+}). XRD technique showed that for the four thermally treated metals at 400°C for 4h, the obtained products are crystalline, meaning, that the XRD spectrum of every sample showed the principal reflections reported in the literature [11, 13, 15].

The XRD diffractograms showed that the $CoWO_4$, $NiWO_4$ and $MnWO_4$ powders present a crystalline monoclinic structure [11], whereas $CuWO_4$ powders exhibit a triclinic crystalline structure [11]. The results show evidence that working with a subsequent thermal treatment at 400°C temperature for 4 h, is possible to achieve the formation of the desired tungstate metal samples.

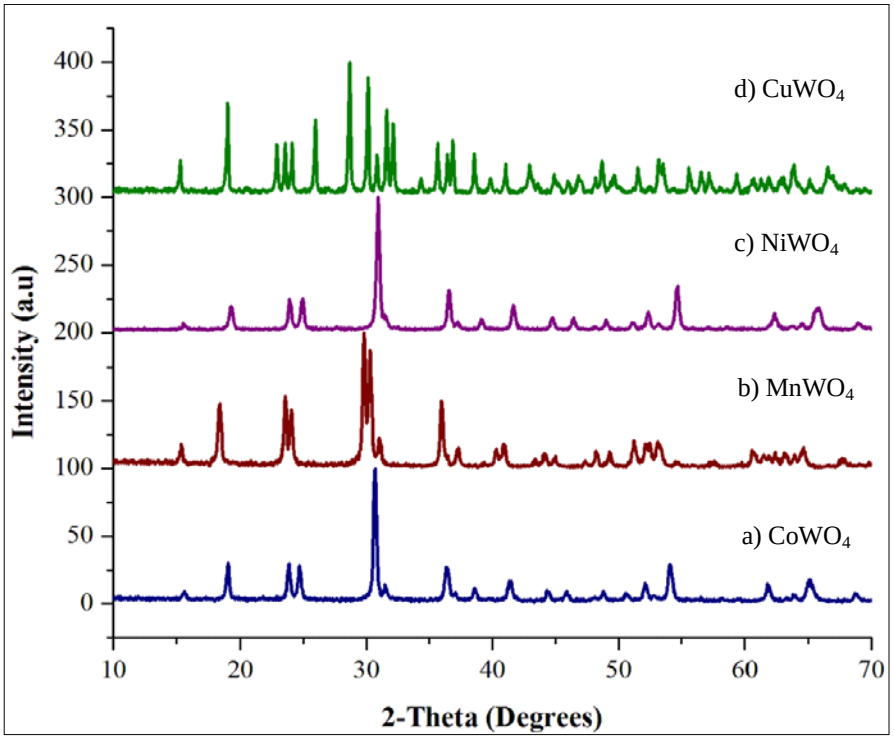

Fig. 2. XRD diffractograms of the synthesized tungstate samples by the dissolution-precipitation technique followed by a thermal treatment at 400°C during 4 h; a) $CoWO_4$, b) $MnWO_4$, c) $NiWO_4$, d) $CuWO_4$.

3.2. UV-Vis Spectra

Figure 3 presents the tungstate diffuse reflectance spectra (UV-Vis) of $CoWO_4$, $MnWO_4$, $NiWO_4$ and $CuWO_4$ samples; results were converted to Kubelka-Munk units [16] through to the following expression:

$$F(R) = \frac{(1-R)^2}{2R} \qquad (2)$$

In order to determine energy band gap of the samples, a lineal region from the inflection point of the diffuse reflectance spectrum is considered, which represents the absorption energy above the border. Extrapolating the lineal slope until the interception to the photonic energy axes (X axes), this point provides the optical band gap value of the material.

The estimated energy band gap values were 2.20 eV (Co), 2.56 eV (Mn), 2.46 (Ni), and 2.24 (Cu), which are similar to the ones reported in the literature for these materials [16-18].

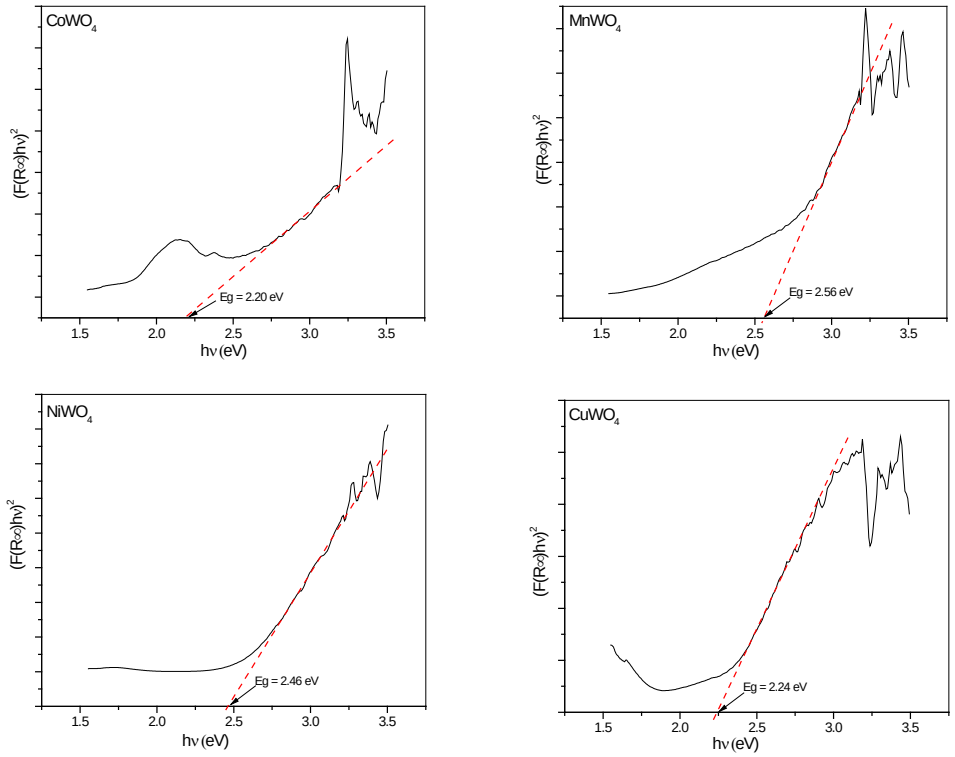

Fig. 3. UV-Vis spectra of samples $CoWO_4$, $MnWO_4$, $NiWO_4$ and $CuWO_4$.

3.3. BET surface area

The specific surface area of the samples was determined by N_2 physisorption. Table 1, presents the materials BET surface areas and band gap energy of the synthesized samples.

The results show the difficulty that exists to obtain large values of surface areas and this will become an issue towards the hydrogen production through water splitting [19].

3.4. Scanning electron microscopy

Scanning electron microscopy provided important information related to their morphology as and well as the apparent particle size and elemental composition present in the samples. Figure 4 shows SEM images of the obtained tungstates treated at 400°C for 4h.

In Figure 4 (a, b and c), similar morphologies were observed, with particles presenting a high degree of agglomeration and large sizes. $CoWO_4$ particles show agglomerates of particles of around 20 µm, while sample $MnWO_4$ show different sizes of agglomerates varying from 10-30 µm. $NiWO_4$ sample show a mixture of small particles of around 5µ to large particle agglomerates of around 30 µm. Finally, sample $CuWO_4$ presents very evident signs of sintering with particles as large as 50 µm with no apparent porosity. While other samples present a rough surface morphology. This behavior can be attributed to the

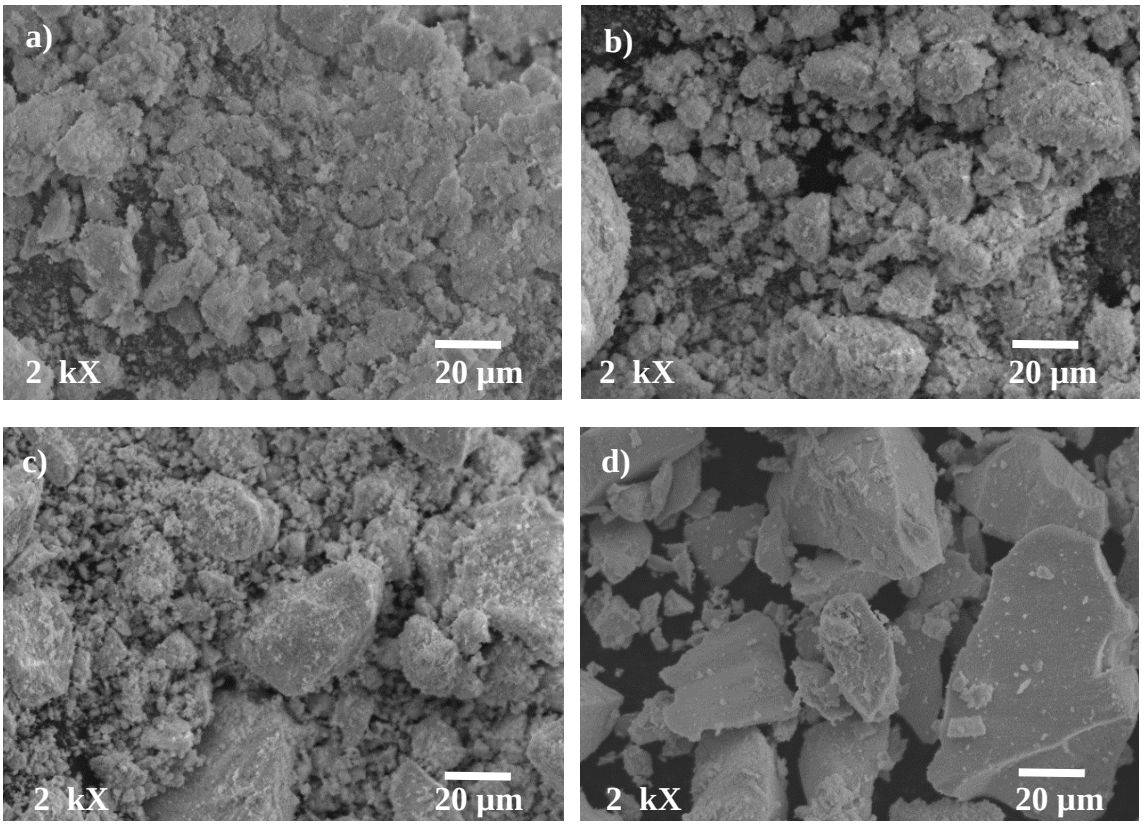

Fig. 4. SEM images of the synthesized tungstates:
a) $CoWO_4$, b) $MnWO_4$, c) $NiWO_4$, d) $CuWO_4$.

intrinsic nature of these materials. Furthermore, the EDS analysis resulted in the expected the molar ratios of the crystalline phase for each sample, thus corroborating the obtained XRD results.

3.5. Photocatalytic evaluation

The photocatalytic evaluation of the different samples was performed by measuring the hydrogen evolution produced by the reaction of the splitting of the water molecule and results are shown in Table 1. The highest hydrogen production was achieved by $MnWO_4$ with 139 µmoles H_2/g_{cat}. While the lowest H_2 produced corresponded to the sample CuWO4 with only 7 µmoles $H_2/g_{cat.}$ Other samples fell in between these values.

The behavior observed in the hydrogen production of the samples can be attributed, presumably, to the particle size here presented, as it was observed in the SEM images, there were agglomerates and large particle sizes, therefore at the irradiation time these particles did not have enough contact time to produce a major hydrogen quantity.

Table 1. BET surface area, band gap energy and hydrogen production for the synthesized samples.

Sample	BET surface area (m^2/g)	Band Gap Energy (eV)	H_2 Production µmoles H_2/g_{cat}
$CoWO_4$	23	2.20	24
$MnWO_4$	22	2.56	139
$NiWO_4$	11	2.46	17
$CuWO_4$	8	2.24	7

4. Conclusion and recommendation

Divalent tungstates of transition metals were successfully synthetized using an effective synthesis method, followed by calcination at 400°C. The photocatalytic activity of $CoWO_4$, $CuWO_4$, $NiWO_4$ and $MnWO_4$ was investigated, obtaining higher H_2 production with compounds $CoWO_4$ and $MnWO_4$. The dissolution-precipitation method allowed to obtain the desired crystalline phase.

However, it is important to optimize conditions to decrease the particle size and increase the available superficial area. The energy band gap of these tungstates fell within the visible light spectrum. Transition metal tungstates can be considered potential candidates for the water splitting of the water molecule under visible light irradiation.

Finally, future work will concentrate in further characterization, to elucidate the decisive properties responsible for the photocatalytic activity of these materials.

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