



Physical and photoelectrochemical properties of the ilmenite NiTiO₃ prepared by wet chemical method and its application for O₂ evolution under visible light

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ABSTRACT

The ilmenite NiTiO₃ prepared by wet chemical method is characterized by thermal gravimetry (TG), X-ray diffraction (XRD), FTIR and Scanning Electron Microscopy (SEM). The oxide crystallizes in the hexagonal symmetry with grains size in the range [200–300 nm]. The BET analysis gives a specific surface area of ~ 4 m² g⁻¹. The UV–vis diffuse reflectance analysis gives a direct transition at 2.57 eV well matched to the solar spectrum. The transport properties exhibit *n*-type semiconductor with an activation energy of 0.11 eV and an electron mobility of 5.82 × 10⁻⁴ cm² V⁻¹ s⁻¹. The physical and chemical characterizations are correlated for the construction of the energy diagram in order to assess the photoelectrochemical properties for the oxygen evolution. The valence band, deriving from O²⁻: 2*p* orbital (2.19 V_{SCE}), is located above the O₂/H₂O potential (~ 1.5 V_{SCE}), allowing O₂-evolution upon visible light (15 mW cm⁻²) and the oxide is photocathodically protected against corrosion. An evolution rate of 0.046 mL mg⁻¹ h⁻¹ is obtained within 20 min upon visible light and under optimal conditions (200 mg of catalyst, pH ~ 3 and 50 °C).

1. Introduction

For a number of years, the interest of ternary oxides and their applications in the solar energy conversion have steadily increased and continue to attract a great interest in many fields including solid fuel cells, sensors, chemical catalysts and dielectrics application [1–4]. The conversion of solar light-to-electrical and/or chemical energy is a topic of great importance because to the depletion of fossil fuels reserves. Indeed, the sun is an inexhaustible energy which becomes important in the modern world because of its versatility, availability and positive contribution to the environment. Among the topics, the photocatalysis is an emergent technique for both the energy supply [5,6] and water purification [7,8]. In this respect, the oxides are advantageous because of their chemical stability and low cost and many researches deal with the crystal field splitting of transition metals with partly-filled *d* levels in the perovskite [9] spinels [10] and delafossites [11]. Our attention was focused on oxides crystallizing in the ilmenite structure and we felt it would be interesting to study NiTiO₃ in the goal to be applied in photocatalysis. The empty e_g orbital forms the conduction band (CB), while t_{2g} level constitutes the sub-band gap states within the forbidden band.

On the other hand, the morphology and surface properties strongly depend on the synthesis method. The conventional techniques for the oxides preparation produce large particles with uncontrolled morphologies. Nowadays, there have been a huge of works on the preparation techniques of nanostructured NiTiO₃ with distinct morphologies like co-precipitation [12], Pechini method [13], sol gel [11] and molten salt [14]. The chemical route produces relatively large active surface areas and does not require high temperatures and long duration.

The aim of this work is focused on the preparation of the ilmenite NiTiO₃ by wet chemical method for its interesting properties like low cost, low calcination temperature, prevention of agglomeration and distinct morphologies. To our knowledge, no previous study on the detailed PEC characterization of NiTiO₃ has been reported and the photocatalytic properties are missing. NiTiO₃ prepared by nitrate route was characterized by physical and electrochemical techniques and successfully tested for the photochemical oxygen evolution under visible light. The photoelectrochemical oxygen evolution is a challenge in the water splitting [15,16]. It is worthwhile to outline that the slowness of O₂ evolution on semiconductor limits the water photoelectrolysis; this is due to the high over-potential which represents

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energy loss but decreases under illumination on NiTiO₃.

2. Experimental

2.1. Materials preparation

We have used the wet chemical method for preparing the NiTiO₃ and all reagents were purchased from Biochem Chemopharma. 0.066 mol of Ni(NO₃)₂·6H₂O and TiO₂ were dissolved respectively in 50 mL of distilled water and 20 mL of concentrated HNO₃ (density 1.375); the solution was mixed at 80 °C until vaporization. The precipitate was dried, ground in an agate mortar and calcined at 500, 800 and 950 °C.

2.2. Characterizations

To investigate the calcination temperature, the thermal analysis (TG) was performed under N₂ atmosphere up to 980 °C with a heating rate of 5 °C/min using a Perkin ELMER TG/DTG STA 6000. The phase purity and the crystal structure were examined by X-ray diffraction (XRD) (Generator Philips diffractometer PW 1729) in the 2θ range (10–80 °) using Cu Kα radiation (λ = 0.154056 nm). The infra-red spectrum was recorded with a Perkin ELMER Spectrum (model 65 FT-IR type ATR Spectrometer). The surface morphology was analyzed with a scanning electron microscope (JEOL-JSM6360) operating at 30 kV. The textural morphology was analyzed by N₂ adsorption with a Micromeritics ASAP2010 and the specific surface area was calculated from the BET analysis. The UV–vis spectrum was obtained at room temperature in the diffuse reflectance mode (R) over the range (200–800 nm) using a Cary 500 spectrophotometer equipped with an integrating sphere.

The electrical conductivity was measured on sintered pellet with GW INSTEK GDM 8255A equipment, using the standard two-probe method in the range (20–300 °C), the temperature was measured with chromel–alumel thermocouple; the ohmic contact was automatically verified. The powder was compacted under 4 kbar and sintered at 980 °C; the pellets showed a theoretical density of 80%. Low contact resistance was required for the transport properties and photoelectrochemical characterization. To this end, a copper wire was fixed on the back pellet with silver cement (work function ~ 4.3 eV) and the pellet was isolated in a glass tube with resin epoxy, leaving a geometrical surface of 1 cm². The working electrode was polished with fine emery papers and thoroughly washed with distilled water. Platinum foil was used as auxiliary electrode and the potential was measured against a saturated calomel electrode (SCE) via a Luggin capillary. The electrochemical tests were performed in a thermostated cell containing a fresh solution of H₂SO₄ (0.01 M) and shielded from daylight with a black box. The solution was flushed free of oxygen by N₂ bubbling and the polarization curves were recorded using a PGZ301 potentiostat (Radiometer) at a scanning rate of 10 mV s⁻¹. The open circuit potential (OCP = -300 mV) must be stabilized before any measurement. The working electrode was illuminated through a flat optical window with a tungsten lamp (200 W). The loss of light intensity by the absorption and reflection was not taken into consideration. The complex impedance spectroscopy (EIS) was measured in the range (10⁻²–10⁵ Hz) using sinusoidal wave signal.

2.3. Photocatalytic activity

The photocatalysis was performed in 2 cm double walled Pyrex reactor, connected to a thermostated bath at 50 °C. 0.2 g of the photocatalyst powder was dispersed in 200 mL of H₂SO₄ aqueous solution (pH ~ 3); the solution was bubbled by N₂ gas under stirring for 30 min. Visible light was provided by three tungsten lamps (200 W) and the intensity (15 mW cm⁻²) was measured with a digital flux meter (Testo 545). The source of imprecision was mainly caused by putting the flux

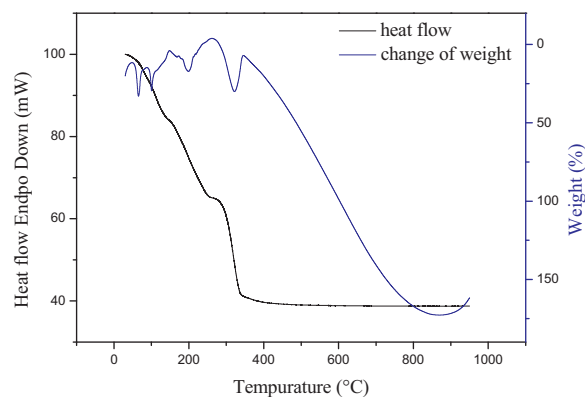


Fig. 1. TG plot of NiTiO₃ prepared by impregnation method and heated up to 980 °C.

meter in slightly different positions. The generated oxygen was analyzed by gas chromatography (Agilent Technology 7890A) equipped with a thermal conductivity detector and quantified volumetrically. The solution was renewed after each test and ionized water was used in the preparation of solutions.

3. Results and discussion

3.1. Physical characterization

Fig. 1 shows the thermal analysis of NiTiO₃. The weight loss occurs from room temperature up to 300 °C, indicating that water exists on both the surface and in the pores of grains. The loss at 310 °C corresponds to the formation of NiO while the formation of NiTiO₃ was observed above 800 °C, indicating a high electrostatic energy of the crystal lattice.

The phases were identified by XRD (Fig. 2), the powder was heated at various temperatures (500, 800 and 950 °C) in order to find the optimal temperature under static conditions. At low temperature, the XRD patterns (Fig. 2a) show the peaks assigned to TiO₂ and NiO matching respectively with to the JCPDS cards (No. 21-1272) and (No. 47-1049). Fig. 2b indicates that at 800 °C, NiTiO₃ appears (JCPDS cards No. 33-0960) with traces of TiO₂ and NiO and further heating up to 950 °C leads to single phase NiTiO₃ (Fig. 2c). Such result corroborates the TG analysis (Fig. 1). The ilmenite NiTiO₃ crystallizes in a hexagonal symmetry (space group $R\bar{3}$) with lattice parameters $a = 0.5002$ nm and $c = 1.3969$ nm matching to the JCPDS cards No. 33-0960. An average crystallite size (D) of ~ 60 nm is estimated from the full width at half maximum:

$$D = 0.94\lambda / (\beta \cos \theta) \quad (1)$$

the structure consists of a close packed hexagonal array of O²⁻ ions with

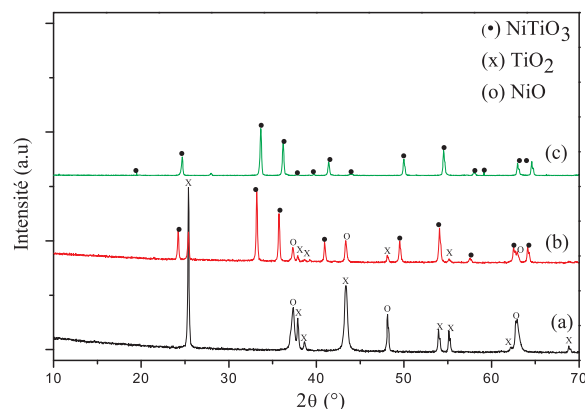


Fig. 2. XRD patterns of NiTiO₃ calcined at: (a) 500 °C, (b) 800 °C and (c) 950 °C.

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