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Preparation and characterization of the brownmillerite $Sr_2Co_2O_5$ as novel photocatalyst in the hydrogen generation

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ABSTRACT

$Sr_2Co_2O_5$ is a semiconductor belonging to the brownmillerite family; it is prepared by nitrate route and the photo-electrochemical properties are assessed for the first time for the photocatalytic hydrogen production. Thermal analysis indicates the formation of the semiconductor phase at 750 °C. An optical transition at 1.10 eV, directly allowed is obtained from the diffuse reflectance spectrum, due to the internal Co^{3+}: *d-d* transition in octahedral coordination. A flat band potential of 0.037 V_{SCE} is determined in KOH solution (0.1 M) from the Mott-Schottky characteristic and the results are relevant for the water reduction. The conduction band of $Sr_2Co_2O_5$ (−0.85 V_{SCE}), deriving from Co^{3+}: *3d* orbital is more cathodic than the potential of H_2O/H_2 couple and hydrogen is successfully evolved under visible light. A rate evolution of 68 µmol (g catalyst)$^{-1}$ min^{-1} at pH ~ 12 and a light-to-chemical energy efficiency of 0.82% are determined.

1. Introduction

Hydrogen is an environmentally friendly energy with a storage capacity of 28 kcal g^{-1} [1,2]; it can be produced cleanly from water and solar light on low cost semiconductors [3,4]. Indeed, the photoelectrochemical (PEC) conversion is simpler to realize than any other type of solar device [5]. The principle is based on the excitation of a semiconductor (SC) by energetic photons ($h\nu > E_g$), generating electron/hole (h^+/e^-) pairs. However the semiconductors like ZnO, SnO_2 or $SrTiO_3$ [6,7] exhibit a good chemical stability but absorb the UV light with accounts for only 4% of the solar flux and are technically unattractive [8]. So, preparing optical semiconducting materials responsive to visible light continues to draw a great attention in photocatalysis [9]. In this respect, the perovsite related compounds were reported to be efficient photocatalysts and have attracted renewed interest in the solar energy conversion [10]. Among the candidates, the brownmillerite $Sr_2Co_2O_5$ belongs to the $A_nM_nO_{3\,n-1}$ family and to our knowledge has not been tested photocatalytically before now [11,12]. With a black color, the oxide can convert a large part of the solar irradiation and exhibits a chemical stability over a wide pH range. In addition, the electronic bands made-up of *3d* orbital, are pH-insensitive and can be judiciously positioned with respect to redox levels in solution by selecting pH [13]. The chemical synthesis produces homogeneous powder with small crystallites size where the electrons have a high probability of reaching the solid/liquid interface [14]. Therefore, we have prepared the oxide from nitrates decomposition and the crystallite size becomes comparable with the diffusion length of the minority carriers of the semiconductor [15].

On the other band, the sunshine duration exceeds 3000 h/year with a solar constant of ~ 1200 W m^{-2} (Algeria) and various alternatives were used for the water splitting, each one has its advantages and shortcomings. The present work deals with the characterization of $Sr_2Co_2O_5$ prepared by nitrate route and its application for the photocatalytic hydrogen production upon visible light [16,17]. The forbidden band of the semiconductor must be greater than the theoretical energy for the water electrolysis (2.46 eV molecule^{-1}), taking into account the over-voltages of oxygen and hydrogen. In addition, the conduction band (CB) must be more negative than the potential of hydrogen evolution reaction (HER) and the valence band less anodic than the O_2/H_2O level and this cannot be achieved on narrow band gap SCs [18]. Hence, a reducing agent is required for the second half reaction. Therefore, the water reduction into hydrogen occurs concomitantly with thiosulfate oxidation which promotes the charges transfer and protects the oxide against photo corrosion [19].

2. Experimental

$Sr_2Co_2O_5$ is synthesized by co-precipitation: $Sr(NO_3)_2$ (Merck, > 99.99%) and $Co(NO_3)_2$, $6H_2O$ (Biochem, 99%) are used as starting reagents. Stoichiometric amounts are accurately weighed, dissolved in water and slowly evaporated on a sand bath. At this level, the thermal analysis (TG) is examined by means of a commercial thermo analyzer

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(Perkin Elmer STA 6000) with a heating rate of 10 °C mn^{-1}. The differential scanning calorimetry (DSC) is performed with NETZSCH DSC instrument. The amorphous precipitate is denitrified on a hot plate; then the powder is well ground in an agate mortar to prevent inhomogeneity, pressed into dense pellets under a pressure 5 kbar and heated at 750 °C with intermediate regrinding, the end product exhibits a black color with a compactness approaching 80%. The phase is confirmed by X-ray diffraction (ITAL STRUCTURES diffractometer APD2000) using Cu Kα radiation (λ=0.154056 nm) over the 2θ range (10–75°). The mean crystallite size is determined from the Williamson Hall plot. The dielectric constant is measured at room temperature by a capacimeter (GW INSTEK GDM-8255A) on sintered pellet.

The chemical stability is tested at various pHs, the absence of Co^{2+} is confirmed by chemical analysis: ~ 10 mg of the powder is dissolved in HCl (5 N) and Co^{2+} is titrated with a UV–Visible spectrophotometer (Shimadzu 1800); Co^{2+} gives with SCN^- a blue complex (Co^{2+}+ 4 SCN^- → $Co(SCN)_4^{2+}$, K_f=5.5×10^{-3}) which absorbs at 619 nm (ε=1770 cm^{-1} mol^{-1} L).

The UV–Visible spectrum of $Sr_2Co_2O_5$ is recorded with a Varian Cary 500 spectrophotometer equipped with an integrating sphere. The electrical conductivity is measured under argon atmosphere using LCR Agilent 4263 B LCR equipment. The ohmic contact of the working electrode is ensured by soldering copper wires onto the back pellets using Ag cement because of its work function (4.26 eV). The pellets are encapsulated in glass holders and isolated by epoxy resin, leaving a surface area of 1.32 cm^2. Prior the electrochemical study, the electrode is polished with emery papers of decreasing roughness (down to 600 mesh). The PEC characterization is done in a standard cell containing KOH (0.05 M) solution as supporting electrolyte and Pt as auxiliary electrode. The potential of the working electrode is controlled by a PGP301 potentiostat (Radiometer analytical) and reported with respect to a saturated calomel electrode (SCE). Nitrogen is continuously bubbled during the electrochemical test to purge air. The light source consists of a tungsten lamp (200 W, Osram) emitting mainly in the visible region; the Mott-Schottky characteristic is plotted at a frequency of 10 kHz. The point of charge zero (pzc) is measured from the equilibrium pH of an aqueous powder solution with a digital pH meter (Schott 825).

A double walled Pyrex reactor (500 mL capacity) is used for the photoactivity; the temperature is regulated at 50 ± 1 °C thanks to a thermostated bath. 125 mg of the catalyst powder are dispersed in 250 mL of alkaline KOH electrolyte ($S_2O_3^{2-}$ 10^{-2} M, KOH: pH ~ 12), daily prepared and stirred magnetically (210 rpm) to preclude the powder sedimentation. Three tungsten lamps (200 W) are used as excitation sources, providing a total intensity of 29 mW cm^{-2}; the photons flux (6.02×10^{19} photons s^{-1}) is measured with a digital light meter (Testo 545). The solution is bubbled with nitrogen under constant purging rate (10 mL mn^{-1}) to eliminate oxygen; after 35 min, the light is switched on. Hydrogen is determined volumetrically in an experimental device described elsewhere [20]. The solution is renewed after each test to avoid any change due to $S_2O_3^{2-}$ oxidation. All solutions are prepared with reagents of analytical quality and distilled water (~ 0.8 MΩ cm).

3. Results and discussion

It is well accepted currently that the morphological properties of solid oxides like the grain size, porosity and specific surface areas are strongly dependent on the synthesis conditions. The brownmillerite $Sr_2Co_2O_5$ is prepared in air and the chemical route is suitable to have regular forms with a narrow size distribution and large active surface areas. The first weight loss (~ 4%) in the TG plot (Fig. 1) is due to the water desorption. Two overlapped weight losses are attributed to the denitrification of strontium (~ 570 °C) and cobalt (~ 640 °C) in agreement with the literature data [21]. The weight levels off above 650 °C, indicating the beginning of the phase formation. This analysis is corroborated by DSC plot (Fig. 2). An estimation of the oxygen content by iodometry was unsuccessful, and approximate value for the oxygen content was obtained from the weight loss observed during the initial heating. The oxygen content (5.03) is based on the mean oxidation state of cobalt, determined analytically.

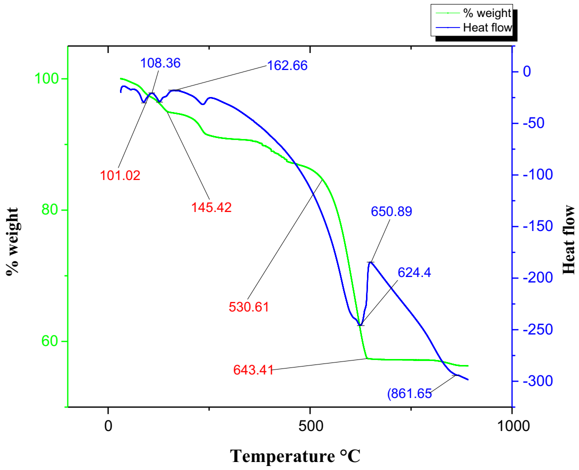

Fig. 1. Combined TDA/TG plots of the nitrate mixture for the preparation of the brownmillerite $Sr_2Co_2O_5$.

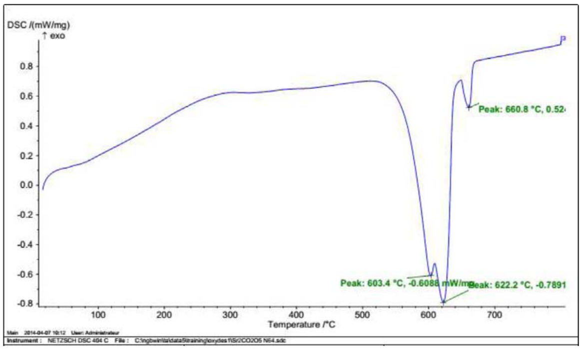

Fig. 2. DSC plot of the of the nitrate mixture for the preparation of $Sr_2Co_2O_5$.

The phase purity is checked by XRD (Fig. 3); the reflection conditions agree with the JCPDS card N° 40–1018 and all peaks are assigned to the brownmillerite $Sr_2Co_2O_5$, crystallizing in a hexagonal symmetry with the lattice constants a =5.485 Å et c =4.137 Å. The structure derives from the double perovskite $Sr_2Co_2O_6$ in which one sixth of oxygen ions are missing and the vacancies are ordered along the [101] direction [22]. The Co-O polyhedra are linked to each other

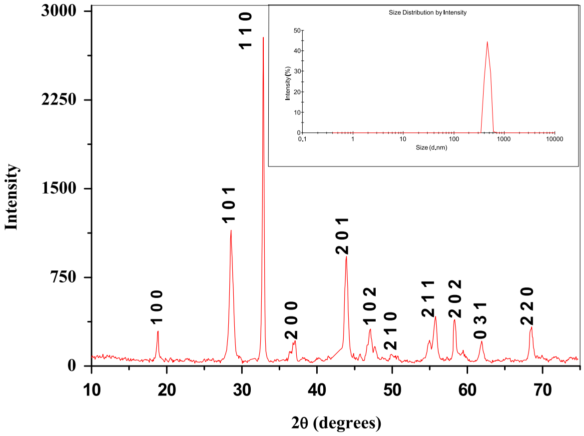

Fig. 3. The X-ray diffraction pattern of $Sr_2Co_2O_5$ prepared by nitrate route. Inset: the sizes distribution.