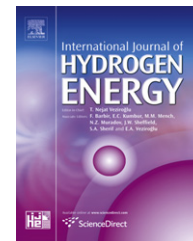


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Photocatalytic hydrogen production over NiO modified silica under visible light irradiation

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ARTICLE INFO

Article history:

Received 23 September 2011

Received in revised form

10 December 2011

Accepted 18 December 2011

Available online 9 January 2012

Keywords:

Hetero-system

NiO/SiO₂

Impregnation

Photoelectrochemical

Hydrogen

ABSTRACT

The novel hetero-system $x\text{NiO}/\text{SiO}_2$ ($x = 0, 4$ and 10%), prepared by impregnation/calcination, is assessed photoelectrochemically for the hydrogen evolution upon visible light. The X ray diffraction show mixed phases with a good crystallinity of NiO, spread uniformly over amorphous silica. The BET measurements give a specific surface area of $\sim 112 \text{ m}^2 \text{ g}^{-1}$ for loaded compounds. The optical properties show strong light absorption of wavelengths shorter than 860 nm . The Mott–Schottky characteristic ($C^{-2}-V$) of NiO exhibits a positive slope, characteristic of n -type conductivity. The flat band potential ($-0.93 \text{ V}_{\text{SCE}}$) is more cathodic than the water reduction level, thus allowing a spontaneous H_2 evolution. The electrochemical impedance spectroscopy reveals the predominance of the diffusion of finite length type and the Nyquist response is decomposed on $R-C$ parallel circuit. NiO plays a key role as sensitizer and the photoactivity increases with increasing its loading. The best performance ($0.2 \text{ cm}^3 \text{ H}_2 (\text{g catalyst})^{-1} \text{ mn}^{-1}$) occurs for $10\% \text{ NiO}$ at $\text{pH} \sim 13.1$ with a light-to-chemical energy yield of 0.19% in presence of SO_3^{2-} as hole scavenger. On the other hand, the decomposition of $\text{S}_2\text{O}_3^{2-}$ is an energy storing process that could be a source of hydrogen from the solar light and the hetero-system is evaluated for the chemical energy storage through the photosynthetic reaction: $(\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + 2\text{OH}^- \rightarrow 2\text{SO}_3^{2-} + 2\text{H}_2, \Delta G_f^\circ = 101.04 \text{ kJ mol}^{-1})$.

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1. Introduction

The photoelectrochemical (PEC) conversion is one of the most attractive processes for the long term storage of the solar energy and it is desirable to make experiments specific to the water electrolysis [1,2]. Hydrogen is no polluting and possesses an energetic power of 285 kJ mol^{-1} , comparable to that of hydrocarbons. It remains a promising alternative to fossil energies and is universally recognized as an environmental friendly fuel [3]. Currently, it is produced by methane

steam reforming and its production from renewable energies offers a clean route for the reduction of the green house gas CO_2 , responsible of the global warming. Accordingly, extensive research on the solar energy is chiefly directed toward reducing materials and manufacturing costs, increasing devices efficiency and protecting against photocorrosion [4]. Various ways exist to decompose water into its constituents; the most conventional one is probably the thermochemical splitting [5]. However, some difficulties subsist in this one step process, namely in achieving high temperature ($>2500 \text{ K}$) and

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in separating the gases. Hence, our investigations are oriented to the PEC conversion and consist of finding novel optically active systems. To have a useful power from interaction photon-semiconductor (SC), three conditions are required: (i) The photons have to be absorbed ($h\nu > E_g$), resulting in electrons being excited to the conduction band, (ii) The charge carriers must be physically separated by the junction electric field, (iii) The carriers must be consumed by redox species before they lose their extra potential, thus preventing the photocorrosion. PEC cells are chemical junctions, specifically designed to convert the sunlight into chemical energy. They are basically characterized by a band bending in the solid side which is typically of 10–20 nm and this appears as positive shortcoming since it permits the separation of electron/hole (e^-/h^+) pairs.

Generally, the optical gap (E_g) and the flat band potential (V_{fb}) of SC oxides are two contradictory factors relevant for the photocatalytic hydrogen production. Indeed, most oxides investigated to date are stable against corrosion but possess either large gap absorbing a small part of the sunlight or have unsuitable flat band potential. It is worth noting that the large gap takes its origin from the low lying valence band (VB), made up of O^{2-} : $2p$ orbital whereas, the conduction band (CB) derives mainly from metal character. To be effective for the water splitting, the gap of SC must be greater than the theoretical dissociation energy ($2.46 \text{ eV molecule}^{-1}$). In addition, the conduction band (CB) should be more negative than the potential of hydrogen evolution reaction (HER).

The usefulness of the photocatalysis has been clearly demonstrated in the past but remains limited to simple oxides. There have been many alternatives aimed to improve the performance of PEC devices [6,7] and a great deal of attention has been paid to composite SC oxides which extend the energy of photo-excitation toward lower values in order to harness the most solar photons [8,9]. The wide band gap SCs like TiO_2 and SnO_2 have been tested successfully as mediators and the photoactivity can be significantly improved when they support narrow band gap SCs [10,11]. After trying a number of binary oxides, NiO is found to be an effective sensitizer which works as electron pump because of the proper position of CB, made up of cationic orbital with a high reducing ability [12,13]. In addition, NiO is inexpensive compared to other oxides and exhibits a chemical stability over a fair pH range. It has been used in many applications like thermal absorber, O_2 -electrodes and electrochromic devices [14,15]. It has an absorption edge at $\sim 3.5 \text{ eV}$ which corresponds to a charge transfer $Ni^{2+} \rightarrow O^{2-}$ and an absorption tail in the visible region attributed to $d-d$ transitions of incomplete d -shell. On the other hand, Chen et al. [16] reported the photocatalytic chromate reduction on the NiO/ TiO_2 junction. The presence of NiO promotes the separation of (e^-/h^+) pairs through the electric junction field and favors the interfacial charge transfer [17,18]. Such enhancement is due to the formation of a short-circuited configuration through the electrolytic solution. However, whereas some heterojunctions with NiO have been studied, only few papers are reported on SiO_2 [19]. In this work, we report on the hydrogen photoevolution over NiO supported on silica. Water is reduced in hydrogen with concomitant oxidation of thiosulfate resulting into an energetically uphill reaction. An

improvement in efficiency for small polaron oxides can be reached by using small crystallites. Indeed, the crystallite size must be comparable with the minority carriers diffusion length and large surface areas as those provided by nano materials are desirable. In such a case, the whole PEC process takes place on a single colloidal particle, eliminating the need for bulk phase diffusion of the reactants. The impregnation method is appropriate in such a case.

2. Experimental

The hetero-systems are prepared by impregnation of SiO_2 (Aerosol 2000) with a solution of $Ni(NO_3)_2$ (Merk, 99%) in the desired proportions (0, 4 and 10%). The technique is useful for obtaining homogeneous oxides at relatively low temperatures. The solutions are stirred for 2 h and then evaporated at 80°C . The powders are heated at 300°C (2 h) and at 500°C (2 h) with a heating rate of $4^\circ\text{C}/\text{mn}$ under air flow (1.2 L h^{-1}). The samples are characterized by X ray diffraction (XRD) using $Mo K_\alpha$ radiation ($\lambda = 0.70930 \text{ nm}$). The average crystallite size (L) is derived from the full width at half maximum (FWHM, $= 0.94\lambda/\beta\cos\theta$) where β is the broadening of the most intense peak. The specific surface areas are obtained from nitrogen adsorption isotherms with a Micromeritics Accu Sorb 2100E type apparatus. In order to have a clean surface, the samples are subjected to vacuum for 4 h. For the stability tests, the nickel concentration is determined by atomic absorption (Perkin Elmer 2380) after dissolving the samples in aqua regia. The morphology is investigated by the scanning electron microscopy (JEOL JSM-6360-LV). The diffuse reflectance spectrum of NiO is recorded with a Cary 500 UV–Visible–NIR spectrophotometer in the range 250–1350 nm, equipped with an integrating sphere accessory.

Electrical contact on NiO pellets, sintered at 500°C , is made by hot soldering copper wires with silver cement. The electrochemical characterization is done in a three compartments cell under nitrogen blanket. The emergency electrode is a Pt electrode and the potentials are given with respect to a saturated calomel electrode (SCE) equipped with a Lugging capillary. The intensity potential $J(V)$ characteristics are plotted with a PGZ301 potentiostat (Radiometer analytical). The capacitance measurements are performed at a frequency of 10 kHz. The complex impedance data are acquired using small amplitude wave signals with a frequency response analyzer in the range (10^{-1} – 10^5 s^{-1}).

The photocatalytic experiments are carried out in a double walled Pyrex reactor of cylindrical shape (600 cm^3). The temperature is regulated at 50°C with a thermostated bath, equipped with a water filter for removing IR light. Typically 250 mg of ($x\% \text{ NiO}/SiO_2$) are suspended in 200 mL of aqueous solution (Na_2SO_3 or $Na_2S_2O_3$, 0.025 M) by magnetic agitation; the pH is adjusted by NaOH with a digital pH-meter (Schott 825) and the solution is deoxygenated in advance for 35 min by bubbling with high purity nitrogen in order to prevent the capture of electrons by dissolved oxygen. Small temperature increase ($\sim 2^\circ\text{C}$) is observed during illumination and a blank correction for pressure and temperature is run. The light source consists of three tungsten lamps ($\times 200 \text{ W}$, Osram) providing a flux intensity of 29 mW cm^{-2} . The photon flux

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