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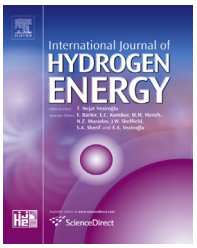

Selective hydrogen sensor for liquefied petroleum gas steam reforming fuel cell systems

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ABSTRACT

Nowadays miniaturized sensors have become more and more important in order to monitor several fields of urban ambient and human life carefully. Low cost synthesis of nanostructured metal oxides for gas-sensing application is therefore of crucial importance for a mass production. Herein, NiO nanostructures were grown and used to realize sensors selective to hydrogen gas in presence of liquefied petroleum gas (LPG), to be used on portable and isolated fuel cell systems. NiO p-type semiconducting nanowires with polycrystalline structure were prepared via an easy, cheap and scalable hydrothermal method. Morphology and crystal structure of the NiO nanowires were characterized by scan electron microscopy, X-ray diffraction, transmission electron microscopy and selected area electron diffraction. The nanostructured material was then tested as hydrogen sensor showing very good performance in terms of sensor response (110%), stability, speed of response and recovery (20 s) and selectivity in presence of LPG (a ratio of 200 times).

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Introduction

Nowadays hydrogen is the most promising fuel to produce energy in transportation and domestic applications. Fuel cells (FCs) operating with hydrogen are one of the most attractive clean energy technologies for stationary and mobile applications because of their high efficiency and zero emissions [1–3]. Small stationary fuel cell systems are designed for applications in remote backup power, especially in isolated off-grid settings. Unfortunately, on-site delivery of hydrogen still has high cost and reliability issues, and its storage is still very difficult as the compression or liquefaction of hydrogen requires high pressure and/or low temperature. Due to these problems, practical applications of FCs require a fuel processing system to convert regular fuels into hydrogen of sufficient purity for FC consumption. As a result, the currently dominant procedure for the hydrogen production is the steam reforming of hydrocarbons [4–7]. Hydrogen production via fuel processing is one of the key issues in the progress of hydrogen-powered fuel cell devices, thus becoming a significant area of catalysis research [8–10]. In the last two decades several light hydrocarbons have been considered for on-board and on-site hydrogen production for fuel cells.

Steam reforming of natural gas is currently the most economical process for the supply of hydrogen [11–13], but

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unfortunately transportation and storage of liquefied natural gas require large energy inputs due to its low liquefaction temperature. Furthermore, transmission and distribution infrastructures for natural gas are generally missing in remote or sparsely populated areas, especially in developing countries. Therefore, an alternative energy source is needed for on-site or on-board hydrogen production for fuel cells [14–16]. LPG is a propane-butane mixture that exists in liquid state at room temperature under moderate pressures (less than 1.5 MPa), readily available from petroleum refineries and conveniently stored and transported [17–19]. With its well established distribution network and safe storage methods, LPG is asserting itself as an attractive fuel for systems in remote areas where a natural gas pipelines are not accessible [20]. Some companies are already active on the market with FC systems working with LPG fuel [21–24], and even using crowdfunding to develop next generation portable LPG-FC systems [25].

This kind of on-board or on-site reforming systems clearly need a feedback on the process efficiency. A low cost, low maintenance miniaturized sensor which can be used to detect hydrogen in atmospheres very rich in LPG is highly useful in such systems: a good control on the steam reforming parameters allows the best combustion conditions to be achieved, fuel economy to be maximized, and exhaust emissions optimized [26–30]. In the last decade metal oxide nanostructures have been extensively studied in order to optimize their physical and chemical properties for many applications, including gas sensing [31,32]. Controlling the size and shape of nanostructured metal oxides is a valid strategy to optimize their performance due to their structure-dependent properties [33–36].

In this paper we are reporting on the growth of nickel oxalate hydrate ($NiC_2O_4 \cdot 2H_2O$) nanowires by the hydrothermal method and their thermal decomposition during annealing at 500 °C, obtaining polycrystalline NiO nanowires [37,38]. Hydrothermal synthetic method has been chosen for its simplicity and low power consumption, while NiO has been used for its excellent chemical stability and pronounced electrical properties [39,40]. Morphology and structure of the as-grown and annealed materials are shown.

The nanosensors are tested for their LPG and hydrogen gas sensing properties, and are proven to be able to detect hydrogen gas [41,42] selectively, even in presence of LPG.

Materials and methods

Synthesis of nickel oxide nanowires

Nickel oxide nanowires have been grown via a two-step procedure consisting in a hydrothermal method followed by a heating treatment at 500 °C. The chemicals used in these experiments were of analytical reagent grade, directly used without further purification. In a typical procedure [43], 0.474 g of $[NiCl_2 \cdot 6H_2O]$ (Sigma–Aldrich, Germany) were dissolved into a mixture of 32 mL ethylene glycol (EG, Sigma–Aldrich) and 18 mL deionized water, in a beaker under constant magnetic stirring at room temperature. After that 0.1206 g of $Na_2C_2O_4$ were added into the beaker and 30 min of continuous magnetic stirring were carried out to ensure a good dispersion of Ni^{2+} ions in the solution. The transparent solution was moved into a teflon-lined stainless steel autoclave of 100 mL, which was sealed and heated for 24 h at 200 °C. After the annealing, the autoclave was let cooling down to room temperature naturally. The obtained product was gathered by centrifugation, washed three times using deionized water and absolute ethanol, and then dried in air. A blue–green powder was obtained as a result.

By calcining at 500 °C this blue–green precursor, consisting in nickel oxalate hydrate $[NiC_2O_4 \cdot 2H_2O]$ long nanowires, polycrystalline NiO nanowires were obtained.

The as-grown nanowires and the calcinated polycrystalline nanowires were characterized and analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The XRD analysis was performed with a Bruker D5005 X-ray diffractometer with $CuK_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA. SEM images were obtained using a JEOL7600 scanning electron microscope operated at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) and selected-area electron diffraction were carried out using a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV.

Sensing devices fabrication

The sensing devices were realized by drop casting nickel oxide nanowires over two interdigitated metal electrodes on a silica substrate. 0.1 mg of NiO nanowires was dispersed in ethanol under ultrasonic vibration for 3 min. The solution was then dropped onto interdigitated comb Pt/Ti electrodes on thermally oxidized piece of silicon wafer. The interdigitated Pt/Ti contacts were deposited onto a thermally oxidized silicon substrate by sputtering and conventional optical lithography technique. The full device is 2 mm × 6 mm, while the two metal electrodes consisted in 18 pairs of fingers, each 800 μm long and 20 μm wide. The gap between two adjacent fingers is 50 μm. After the deposition of nickel oxide nanowires, the sensor was heated up to 500 °C at a rate of 1.0 °C min^{-1} in a furnace and then kept for 2 h in order to increase stability and adhesion between nickel oxide and metal electrodes.

Gas-sensing measurements

The NiO nanowires sensing performance were measured under dynamic conditions: the dilution (dry air) and the tested gas were always flowing through the sensing chamber at a total flow rate of 500 sccm. The equipment was home-built and incorporated a test chamber, a sensor holder which could be heated up to 500 °C and some mass flow controllers (connected to high purity calibrated bottles).

The device resistance was measured using a Keithley 2400 multimeter connected to a data acquisition system (LabView, National Instruments). The samples, biased with a DC voltage of 1 V and operated in air, showed a good ohmic behaviour which a negligible metal–semiconductor resistance. The sensor percentage response S% along this paper is defined as $S\% = (R_{gas} - R_{air})/R_{air} \cdot 100$, where R_{gas} and R_{air} are the resistance of the device with analyte (reducing) gas or without it,

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