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Synthesis and characterization of SnO_2-HMD-Fe materials with improved electric properties and affinity towards hydrogen

N. Bouazizi [a,b], R. Bargougui [c], T. Boudharaa [d], M. Khelil [e], A. Benghnia [b], L. Labiadh [c], R. Ben slama [b], B. Chaouachi [b], S. Ammar [c,f], A. Azzouz [a,*]

[a] Nanoqam, Department of Chemistry, University of Quebec at Montreal, Montreal, QC, Canada H3C 3P8
[b] Research unit: Environment, Catalyzes and Process Analysis, ENI,G University of Gabes, Tunisia
[c] Department of chemistry, Faculty of Sciences, University of Gabes, Tunisia
[d] Useful materials valaorization laboratory, Borj Cedria, Tunis, Tunisia
[e] Laboratory of Materials Physics and Nanomaterials Applied at Environment (LaPhyMNE), FSG-University of Gabes, Tunisia
[f] Departement of chemistry, Faculty of Sciences, University of Carthage Bizerte, Tunisia

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ABSTRACT

Tin oxide (SnO_2) was functionalized by hexamethylenediamine (HMD) grafting and incorporation of iron nanoparticles (Fe-NPs) and, then, fully characterized by X-ray diffractometry, transmission electron microscopy, diffuse reflectance spectrometry, FTIR spectrophotometery, photoluminescence spectroscopy and complexes impedance spectroscopy measurements. The covalent surface-grafting of HMD within mesopores was confirmed by the results from Fourier-transformed infrared spectroscopy. XRD and TEM study showed a dominant tetragonal structure. Fe-NPs were finely dispersed inside mesopores, producing a slight structure compaction. The crystallite size decreased in the presence of HMD and Fe-NPs. Photoluminescence (PL) insights revealed the presence of oxygen vacancies and the PL intensity was found to strongly depend on HMD grafting and Fe-NPs insertion. The incorporation of both Fe-NPs and HMD grafting appear to be responsible for electrical properties improvement. This material displayed an unprecedented surface affinity factor towards hydrogen of 8.5 μmol m^{-2} at ambient temperature and pressure. This was attributed to the contribution of both physical and chemical hydrogen adsorption, and to the presence of fine Fe-NPs. These properties open promising prospects for green energy storage.

1. Introduction

Metals are known to display electric features, redox behavior and affinity towards hydrogen. Metal (0) dispersion in the form of fine particles is expected to induce such properties, resulting in interesting materials that can act as semi-conductors [1], hydrogen adsorbents [2] and sensors [3]. For instance, mesoporous nanosheets decorated with palladium nanoparticles exhibited sensing properties for hydrogen for diverse purposes, including H_2-monitoring in radioactive environments [4–7].

In this regard, transparent conductive oxides have attracted considerable attention due to their potential applications in electrical, optical, electronic and electrochemical devices. Among them, tin oxide (SnO_2) is a semiconductor with a wide band gap (Eg=3.8 eV) and photoactive material [8], gas sensor [9,10] and also a potential attractive semiconductor matrix for hosting transition metal ions [11,12]. SnO_2 nanoparticles can be prepared by numerous methods [13–15]. The sol–gel method requires less sophisticated and cost-effective procedure for producing highly performant materials.

Doping with metal is expected to improve the sensitivity of the metal oxide and its surface area. Transition metal doped SnO_2 received considerable attention, being regarded as promising materials for their properties and applications. The incorporation of Fe into SnO_2 may be a judicious route for inducing ionic conductivity and envisaging sensors applications. Fe-doped SnO_2 was already found to display higher gas sensitivities than its unmodified counterpart [16]. In addition, some factors such as the structure morphology and the presence of defects could markedly influence the iron site distribution as well as their specific magnetic interactions [17]. Knowledge regarding the local environment of the dopant is an essential requirement to understand how the magnetic order arises in such matrices [17,18]. High dopant dispersion often requires an improved diffusion of the metal source, and fine oxide powders are suitable for such a purpose. However, SnO_2 in powder form, like any other metal oxide, has a strong tendency to re-aggregate into bulky clusters due to strong adhesion forces. An improvement in this regard can be

* Corresponding author.
E-mail address: azzouz.a@uqam.ca (A. Azzouz).

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achieved by grafting organic moieties on the external surface of the oxide particles. This should also generate porosity within the entanglement of the organic chains and thereby contributing to a higher dispersion and stabilization of the dopant on the external surface.

In the present work, an effective route for the synthesis of such a material involved SnO_2 functionalization by hexamethylenediamine (HMD) followed by the incorporation of iron nanoparticles (Fe-NPs). The interest devoted to iron nanoparticles is justified by their specific sensing properties [19,20]. These properties of SnO_2-HMD-Fe allow envisaging potential applications as efficient material for electrodes [21]. Attempts were further made to assess not only the electrical properties of the surface but also the affinity towards hydrogen. Both properties converge towards the preparation of materials that can act as semi-conductors or hydrogen sensors or both simultaneously. To demonstrate this strategy, our approach involved a specific succession of characterization technique and adsorption test. Photoluminescence measurements provide valuable data on the band gap energy and the presence of electron acceptors and donors. To the best of our knowledge, the possible application of SnO_2-HMD-Fe as potential hydrogen sensor or adsorbent has not been tackled so far. The hydrogen sensing properties were investigated with respect to their response at ambient conditions.

2. Experimental

2.1. Material synthesis

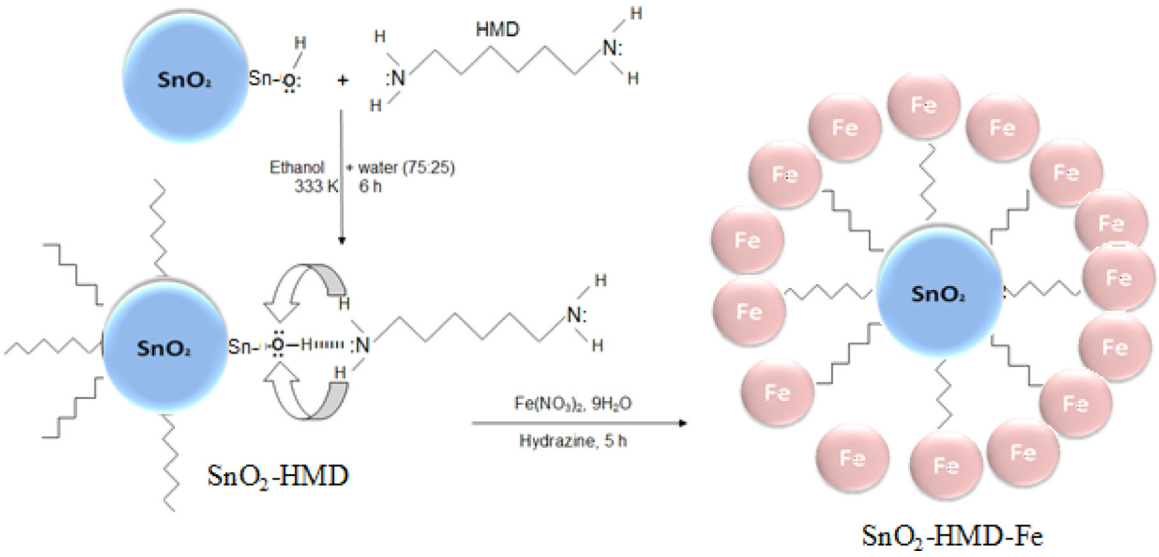
SnO_2 powders were synthesized by co-precipitation of appropriate amounts of stannic tetrachloride hydrated ($SnCl_4.5H_2O$) previously dissolved in 150 ml of deoxygenated distilled water in the presence of 50 ml of NaOH at 70 °C for 4 h. The resulting precipitates were separated by centrifugation and repeatedly washed with deionized water. Total removal of chloride was monitored though periodical tests with an aqueous $AgNO_3$ solution. The final pure SnO_2 powders were dried at 90 °C overnight and then impregnated with hexamethylenediamine in a water-ethanol solvent mixture (25:75 Vol) at 80 °C for 6 h. The SnO_2-HMD material obtained was repeatedly washed and filtrated, then dried at 323 K overnight. Fe-NP dispersion was achieved using $(Fe(NO_3)_3.9H_2O)$ as precursor in toluene (99.5%, $d=0.865$ g mL^{-1}) in the presence of hydrazine as the reducing agent. The mixture turned black after 5 hours under continuous stirring at room temperature, indicating the formation of Fe-NPs within SnO_2-HMD. The final SnO_2-HMD-Fe material was dried at 80 °C for 6 h and then stored in sealed enclosure containing dry and O_2-free nitrogen (Scheme 1).

2.2. Material characterization

The as-prepared samples were previously characterized through powder X-ray diffraction (XRD) (Siemens D5000 X-ray diffractometer and a Cu-Kα radiation at $\lambda=1.54056$ A°), Fourier transform IR spectroscopy (KBr cell, Fourier FTIR equipment and infrared spectroscopy (NICOLET IR200) and transmission electron microscopy (TEM, JEM-200CX). The samples for TEM were dispersed in EtOH under ultrasound exposure and few drops of the resulting suspension were deposited onto the TEM grid. In a second step, the band gap was assessed using diffuse-reflectance UV–vis spectra (DRS) obtained on a Sinco S-4100 spectrometer. Photoluminescence spectra were recorded at room temperature using a fluorescence spectrophotometer (Jobin Yvon FL3-21) with an Xe lamp (450 W) at 325 nm. N_2 adsorption–desorption measurements were performed at 77 K on a Micromeritics ASAP 2020 instrument. All samples were outgassed at 80 °C for 5 h before analysis.

Electrical measurements were performed using a two electrode configurations. The samples were compacted into pellets of 8 mm diameter and 1 mm thickness under a 3 t cm^{-2} uniaxial pressure. Electrical impedances, i.e. the variations of both real (Z′) and imaginary (Z″) parts of the complex impedance ($Z^*=Z'-iZ''$), were assessed in the frequency range [40 Hz to 100 kHz] with a TEGAM 3550 ALF automatic bridge at room temperature.

Hydrogen adsorption tests were conducted by contacting, at room temperature and normal pressure, 0.5g of adsorbent, previously dried overnight at ambient temperature and pressure, with 10 mL of pure dry air-free hydrogen within a 20 mL sealed enclosure containing dry air-free nitrogen. The amount of adsorbed hydrogen was assessed through triplicate measurements of the volume change within a capillary glass tube having a 0.25 mm internal diameter containing a colored drop of oil serving as mobile hydraulic cap.



Scheme 1. Synthetic strategy towards SnO_2-HMD-Fe for hydrogen capture.