Journal of Alloys and Compounds 668 (2016) 65–72

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Structural, optical and magnetic properties of Ni doped SnO_2 nanoparticles

Petronela Pascariu (Dorneanu) [a, b, *], Anton Airinei [a], Mircea Grigoras [a], Nicusor Fifere [a], Liviu Sacarescu [a], Nicoleta Lupu [c], Laurentiu Stoleriu [b]

[a] "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, Iasi 700487, Romania
[b] Faculty of Physics, "Al. I. Cuza" University, Iasi 700506, Romania
[c] National Institute of Research and Development for Technical Physics, Iasi RO-700050, Romania

ARTICLE INFO

Article history:
Received 29 October 2015
Received in revised form
4 January 2016
Accepted 22 January 2016
Available online 27 January 2016

Keywords:
Nanoparticles
Tin oxide
Fluorescence
Magnetic properties
TEM
X-ray diffraction

ABSTRACT

Nickel doped tin dioxide nanoparticles have been obtained by co-precipitation procedure. X-Ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive x-ray analysis (EDX), UV–VIS absorption spectroscopy, fluorescence spectroscopy and room temperature magnetization measurements were performed to study the crystal structure, morphology, elemental analysis, photoluminescence and magnetic properties of Ni doped SnO_2 nanoparticles. TEM results depict the formation of tetragonal shaped and small sized nanoparticles of the diameter of about 10–40 nm. The emission spectra of the SnO_2 and Ni doped SnO_2 nanoparticles present three main regions, a broad emission band located between 320 and 395 nm due to the free exciton recombination; four emission bands at about 412, 438, 450 and 475 nm, respectively, and the green emission bands of low intensity at 520 and 533 nm, appearing due to the and impurities and structural defect states. The magnetic measurements revealed that the Ni doped SnO_2 powder samples presented ferromagnetic properties. The estimated values of the saturation magnetization (M_s) and the coercive field (H_c) are found to be $5 \cdot 10^{-4}$ emu/g and between 83 ÷ 96 sOe (depending on the amount of Ni in the sample), respectively.

1. Introduction

Nanomaterials and nanostructures are under extensive investigation in modern materials science due to their interesting properties. Nanocomposite materials such as nanoparticles, nanowires, nanorods and nanobelts have attracted considerable attention in the field of materials because of their peculiar structure characteristics and size effects [1]. Oxide based diluted magnetic semiconductors are extensively studied both experimentally and theoretically due to their potential applications namely storage devices, optoelectronics, nanoelectronics and photonic devices. These materials may play an important role in future spintronic devices which manipulate both charge and spin [2,3].

The interest in the optical and physical properties of metal oxides (SnO_2, TiO_2, CdO and ZnO) has significantly increased due to their desired applications in optical and electronic fields, especially when they are doped with magnetic components. Tin oxide (SnO_2) with rutile structure is a promising functional n-type semiconductor material with a wide band-gap ($E_g = 3.65$ eV at 300 K), and it has been investigated for various applications such as gas sensors, solar cells, transparent conductive electrodes, spintronics and biosensor etc. [4–8].

Generaly, the presence of oxygen vacancies and the addition of some impurity atoms in the SnO_2 can lead to an improvement of the electrical and optical properties of the material [9]. Also, by the doping of SnO_2 with transition metal ions (Mn, Fe, Ni, Co, etc) this can become a good candidate for ferromagnetic semiconductors because of its large number of structural geometries with an electronic structure that can have metallic, semiconductor or insulator character [10] and potential applications (magnetic devices and ultra-low power transistors, gas sensors, dye-base solar cells, optoelectronic devices, electrode materials, and catalysts). Ni doped SnO_2 nanoparticles are of great interest for various applications, especially in optoelectronics; spin polarized light emitting diodes

* Corresponding author. "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, Iasi 700487, Romania. Tel.: +40 232 217 454; fax: +40 232 211 299.
E-mail addresses: pascariu_petronela@yahoo.com, dorneanu.petronela@icmpp.ro (P.P. (Dorneanu)).

http://dx.doi.org/10.1016/j.jallcom.2016.01.183
0925-8388/

(LEDs), photovoltaics and sensors. Room temperature ferromagnetism was reported in transition metal ions (Ni, Co, Cr, Fe) doped ZnO [11] TiO_2 [12], CuO_2 [13] and SnO_2 [14]. Magnetic properties have been reported in Fe, Mn and Co doped SnO_2 by many research groups [15–17]. Sharma et al. [14] reported that the band gap energy of Ni doped SnO_2 samples decreases with increasing Ni concentration and also, a higher saturation magnetization was observed in low concentration Ni doped tin oxide nanoparticles. Kuppan et al. [18] studied the influence of Ni doping level on structural, optical, and magnetic properties of some powder samples of Ni doped SnO_2 obtained by solid state reaction method.

For preparation of such nanoparticles (Ni doped SnO_2), co-precipitation method has emerged as a novel economically viable technique with large-scale production capabilities. Also, this method has the advantage of a precise control over the stoichiometry, low temperature synthesis, high purity and high chemical homogeneity. SnO_2 doped with Ni using co-precipitation method has been less investigated with few reports available [19,20].

Taking into account the above mentioned, Ni doped SnO_2 nanoparticles were obtained by chemical co-precipitation method. Also, a detailed study of effect of Ni doping on the structural, photoluminescence and magnetic properties of SnO_2 nanoparticles was performed.

2. Experimental

2.1. Materials

Tin chloride, $SnCl_2\cdot 2H_2O$, 2-propanol of spectrophotometric grade were purchased from Sigma Aldrich Chemical Co. and nickel chloride, $NiCl_2\cdot 6H_2O$ of analytical grade from Reactivul Bucuresti and were used without further purification.

2.2. Synthesis procedure

Ni doped SnO_2 nanoparticles were prepared by the co-precipitation method using as starting materials for synthesis $SnCl_2\cdot 2H_2O$ and $NiCl_2\cdot 6H_2O$. In a typical procedure 0.1 M hydrated tin chloride was dissolved in 20 mL double-distilled water under vigorous stirring for 30 min. Then, in this solution required amounts of $NiCl_2\cdot 6H_2O$ were added and dissolved. Finally, aqueous ammonia (1M) was dropped in the mixture solution with constant stirring at 30 ÷ 40 °C for 1 h. The precipitate was filtered and washed thoroughly with distilled water and ethanol and then dried at 100 °C for 24 h. The dried powder was further calcined at 600 °C for 3 h to obtain Ni doped SnO_2 nanoparticles. In this work, series of samples labeled for brevity NS4–NS8, containing different Ni/Sn molar ratios were prepared as it is shown in Table 1.

2.3. Characterization techniques

Phase identification and crystallite size determination were carried out by X-ray diffraction (XRD) method, using a DRON-2 diffractometer (CuKα radiation, λ = 1.54182 Å). XRD data were collected in the 2θ range from 20 to 80° using step scan mode with step width of 0.02°. The chemical composition was determined with an energy dispersive X-ray (EDX) system attached with the scanning electron microscope Quanta 200 at an acceleration voltage of 15 kV. An X-ray photoelectron spectrometer (KRATOS *Axis Nova*) was used to probe the chemical state of Ni doped SnO_2. Transmission electron microscopy (TEM) images were obtained with a Hitachi High-Tech HT7700 transmission electron microscope operating at 120 kV. The powder nanoparticles were suspended in ethanol and homogenized under magnetic agitation for 30 min. One drop from this suspension was put on a copper grid and let dry for several minutes in air at room temperature. Optical absorption spectra were recorded on a SPECORD 200 Analytik Jena instrument with 10 mm quartz cells in 2-propanol solutions. The diffuse reflectance spectra were measured on thin films deposited onto quartz substrates by the evaporation of 2-propanol solutions with an integrating sphere using Shimadzu sss-3600 spectrophotometer. Fluorescence spectra were aquired using a Perkin Elmer LS55 luminescence spectrometer in 10 mm quartz cells with an excitation wavelength of 300 nm at room temperature. The SnO_2 and Ni doped SnO_2 nanoparticles obtained by calcination at 600 °C were added in a quartz cuvette with 2-propanol solution. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM).

Table 1
Series of Ni doped SnO_2 nanoparticles with different molar ratios of Ni/Sn and band gap energy values.

Sample code	Molar ratio Ni/Sn	E_g (eV)
NS4	0.185	3.85
NS5	0.202	3.89
NS6	0.300	3.99
NS7	0.415	3.99
NS8	0.000	4.00

3. Results and discussion

3.1. Structural characterization

The typical XRD patterns of undoped and nickel doped SnO_2 nanoparticles calcined at 600° C are shown in Fig. 1. All diffraction peaks can be assigned to the tetragonal rutile structure of SnO_2 with lattice constants of a = 4.690 Å and c = 3.166 Å, which confirmed by reference pattern JCPDS 880287. Ni doping does not modify the tetragonal structure of SnO_2. The major peaks appear at 2θ = 26.86°, 34.14°, 38.22°, 39.12°, 52.00°, 54.92°, 58.04°, 62.18°, 64.88°, 66.22°, 71.52° and 78.92° and can be associated with (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 1), (2 2 0), (0 0 2), (3 1 0), (1 1 2), (3 0 1), (2 2 0) and (3 2 1) planes, respectively. No characteristic peaks of some impurities were observed in diffractograms, indicating the single phase formation. A matching of the observed and standard (hkl) planes confirmed that the product is SnO_2 with a tetragonal structure, which are in good agreement with the literature values

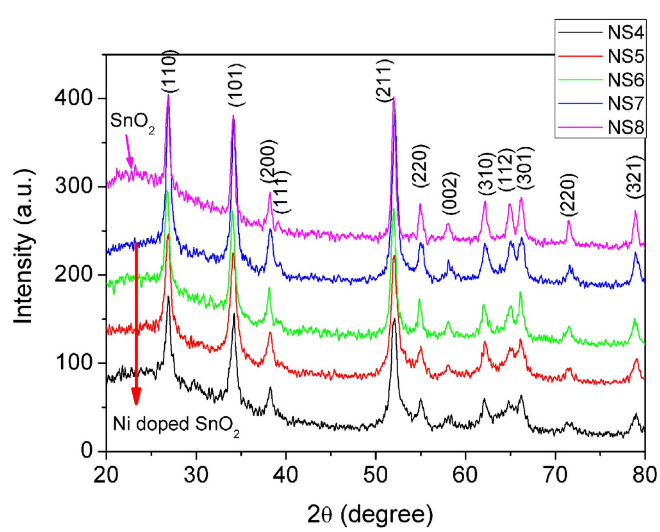

Fig. 1. XRD diffactograms of undoped and nickel doped SnO_2 nanoparticles.