Journal of Molecular Structure 1100 (2015) 562–569

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Structural, morphological and gas sensing study of palladium doped tin oxide nanoparticles synthesized via hydrothermal technique

Davender Singh [a, *], Virender Singh Kundu [b], A.S. Maan [a]

[a] Department of Physics, Maharshi Dayanand University, Rohtak 124 001, India
[b] Department of Electronic Science, Kurukshetra University, Kurukshetra 136 119, India

ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
31 July 2015
Accepted 3 August 2015
Available online 8 August 2015

Keywords:
Pd:SnO_2
Nanoparticles
Hydrothermal
XRD
SEM
EDX
Gas sensing response

ABSTRACT

In this article pure and Pd-doped SnO_2 (Pd:SnO_2) nanoparticles with various mol% Pd have been synthesized by hydrothermal technique. To characterize the morphology, crystallinity, and structure of the SnO_2 and Pd:SnO_2 X-ray diffraction (XRD) and scanning electron microscope (SEM) studies were used. XRD analysis reveal that all nanoparticles of different doping concentration are highly polycrystalline in nature. Pd-doped SnO_2 crystals existed mainly as tetragonal rutile structure. The particle size of the nanoparticles was calculated by using the Scherrer formula and was found in the range of 8–27 nm. The SEM images of the studied nanoparticles confirms the existence of very small, homogeneously distributed, spherical and extremely crystalline nanoparticles. EDX analysis confirms the presence of palladium. The Fourier transform infrared spectroscopy (FTIR) study confirmed the formation of Sn–O phase and hydrous nature of the pure and Pd-doped SnO_2 nanoparticles. The gas sensing response of SnO_2 and Pd:SnO_2 nanoparticles was studied towards different reducing gases at different operating temperatures. Among all samples under study, 0.20% Pd-doped SnO_2 exhibits best response towards different gases. 0.20% Pd-doped SnO_2 shows maximum response 88% to ethanol, 80% to CO and 78% to H_2 at concentration of 100 ppm respectively at different operating temperature within the measurement limit.

1. Introduction

Metal oxide nanostructures are of extensive interest for expansion of nanoelectronic devices, solar cells, photocatalysts, gas sensors etc [1,2]. These metal semiconductor oxides are essential to smart the functional materials due to two exclusive characteristics one is deviation in valence state and other is oxygen vacancies. Among these metal oxides, tin oxide is exciting as it is a binary semiconductor oxide with a great band gap (Eg = 3.6 eV) that can be modified by making use of a doping material. The sensitivity of tin oxide is estimated to enhance by developing in the form of nanoparticles due to the increase in the surface to volume ratio. Research on the fresh preparation methods for tin oxide (SnO_2) nanostructures and the doping effects on surface properties as well as on sensing properties are key steps to obtain gas sensing materials with high performance [3–5]. Presently much concentration has been centered on correlation between the nanostructures and their activity [6,7]. Recently through the high level research it has been observed that sensing properties at working temperature, selectivity, and thermal stability can be greatly enhanced by controllable preparation with proper doping of metals [8–14]. Pd-doping is constantly measured and evaluated by effectual method to improve the sensitivity and decrease the operating temperature. Choi SW et al. [15] showed that bimetallic Pd/Pt nanoparticle-functionalized SnO_2 nanostructured have a fast response and recovery time to NO_2. Kamiuchi et al. [16] investigated that Pd doped SnO_2 exhibits reduced catalytic properties. The well dispersed palladium deposits correspond to huge numbers of dynamic sites. The structural changes of large particles and particle with core–-shell structure lead to the deterioration of the catalytic activity. Trung et al. [17] showed by decorating Pd nanoparticles on surface of SnO_2 nanostructures that CO gas sensing performance can be enhanced and can be sensed the very low concentration of CO gas with good response-recovery time and high stability. Tian et al. [18] explained that Pd-doped flower-like SnO_2 sensors shows a low detection limit, low operating temperature, and high sensing response value towards toluene, this one is endorsed by catalytic action of Pd. Rui-qin et al. [19] showed that grain sizes of SnO_2 nanoparticles changed after doping of Pd. Studies on the thermal

* Corresponding author.
E-mail address: davender_kadian@rediffmail.com (D. Singh).

http://dx.doi.org/10.1016/j.molstruc.2015.08.009
0022-2860/

stabilities showed Pd-doping could contain the growth of grain sizes below 500 °C while the grain growth was enhanced with rise in temperature above 700 °C and the best 2.5% of Pd has recommended for better sensitivity and thermal stability. Jiang Ma et al. [20] showed Pd-doped nanoribbons exhibits much improved gas sensing property towards acetone, ethanol etc gases in comparison to the pure SnO_2 nanoribbons. Masoud Salavati-Niasari et al. [21] used a new precursor, [bis (2-hydroxy-1-naphthaldehydato) tin (II)]; ([Sn (HNA) 2]), in thermal decomposition process for the synthesis of tin oxide (SnO_2) nanoclusters. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy etc. Fatemeh Davar et al. [22] prepared pure tin oxide (SnO_2) nanoparticles via thermolysis of tin phthalate and tin oxalate in the presence of oleic acid (OA) as solvent. Oleic acid (OA) was employed as an organic solvent which can be applied to control particle growth and to stabilize the particles. Synthesized SnO_2 nanoparticles found to have a pure orthorhombic phase with average size about 12 nm.

In this present work, author synthesize and characterized pure and Pd–SnO_2 nanoparticles by hydrothermal technique to analyze further in what way the doping of Pd can modify the properties of SnO_2 nanomaterials.

2. Experimental

2.1. Synthesis of pure and Pd-doped SnO_2 (Pd:SnO_2)

The pure and Pd-doped SnO_2 nanoparticles have been synthesized by hydrothermal method. The tin chloride (hydrous $SnCl_4.5H_2O$, 98% Hi Media) and palladium chloride (anhydrous $PdCl_2$ 99%, Sigma–Aldrich) of AR grades have been used as starting material for the synthesis of Pd-doped SnO_2 nanoparticles. xPd(1−x)SnO_2 with various mol% (e.g. x = 0, 0.05, 0.1, 0.15 and 0.20%) nanoparticles were successfully prepared by dissolving required amount of $SnCl_4.5H_2O$ in 50 ml DI (de-ionized) water under constant stirring and $PdCl_2$ in 15 ml DI water separately with addition of sufficient amount of HCl drop wise till the complete dissolution of Palladium in distilled water. Then, the solution of $PdCl_2$ has dissolved drop wise to the solution of tin chloride under constant stirring at 60–70 °C for 90 min. After that sufficient amount of aqueous ammonia (NH_4OH) has added to the above solution as reducing agent till the formation of perfect gel. The dropping rate must be well controlled for the chemical homogeneity. The gel is transferred to teflon lined stainless steel autoclave and heating treatment of synthesized nanoparticles were conducted at 100 °C for 24 h. The gel is filtered and washed (3–4 times) with DI water and dried at 80 °C for 6–7 h in order to remove water molecules Finally, palladium tin oxide nanopowders were obtained after annealing at 400 °C for 5 h. The complete procedural flow chart is shown in Fig. 1.

2.2. Characterization

2.2.1. Structural and morphological characterization

The detailed characterization of pure and Pd-doped SnO_2 was carried out using XRD, SEM with EDX, FTIR and gas sensing analyzer. The XRD patterns were taken by using Cu Kα X-ray source having fixed wavelength, λ = 1.5406 Å radiation at 2θ values between 20^0 and 70^0. Rigaku X-ray diffractometer with the obtained XRD patterns are given in Fig. 2 and the average grain size of all pure and Pd-doped SnO_2 nanoparticles was calculated by using the FWHM of peaks according to the Scherrer equation [23,24].

$$D = 0.94\lambda/\beta Cos\theta$$

where D is average crystallite domain size perpendicular to reflecting planes, λ is wavelength (1.5406 Å) of X-rays used, β is broadening of diffraction line measured at half of its maximum intensity (in radian), full width at half maximum, and θ is angle of diffraction.

The surface morphology and elemental composition were observed by Scanning Electron Microscope (SEM) and EDX. The SEM images of pure and Pd-doped SnO_2 are shown in given Fig. 3.

The compositions of Pd-doped SnO_2 were examined by EDX as shown in Fig. 4.

The FTIR spectra in range 500–4000 $cm^{-1}$of pure and Pd-doped SnO_2 are shown in Fig. 5. The FTIR study was completed with Thermo Scientific model no. Nicolet™iS™ 50 FT-IR spectrometer over the range 500–2000 cm^{-1}.

2.2.2. Sensing characterization

To study the gas sensing behavior of samples, the fine powders of both, pure and Pd-doped tin oxide samples were pressed into pellets of 10 mm diameter and 2.5 mm thickness at a pressure of 25 Mpa separately using a hydraulic press. These pellets were calcinated at around 500 °C for 2 h in air and then both side faces were polished and coated with conducting silver paste used for making ohmic contacts on the two flat surfaces of pellets. For electrical measurements, pellet was mounted in a specially designed chamber (home-made two-probe assembly) which was inserted coaxially inside a resistance-heated furnace. The fixed amount of gas (CO, H_2 or Ethanol) was injected into chamber of gas sensing system where sensor was placed. The dc resistance of sample was measured using a Keithley-617 electrometer. The sensor characteristics were recorded by measuring resistance in presence of gas and in air at different temperatures in the range 50–300 °C. The concentration of gas and temperature of chamber are measured by mass flow meters and a thermocouple (K-type Chromal-Alumna) respectively, attached to the sensor.

The sensing of various gases is mainly a surface phenomenon and is managed by the adsorbed oxygen species. The doping with Pt, Pd and Ru [25–28] improves various oxygen species and as result an enhancement in the gas sensing characteristic achieved.

The gas sensitivity of pure and Pd-doped SnO_2 pallets was measured for different concentration of gases at different temperature. The 50 and 100 ppm of ethanol, hydrogen (H_2) and carbon mono-oxide (CO) gases were used as target gases. Initially the resistance of pallets was determined in presence of air. On exposing pellet samples to these target gases, pellet resistance was found to decrease for all three gases. Sensor response (S) has been defined as the ratio of change in pellet resistance to pellet resistance in air (at constant temperature) and is given by the equation [29].

$$S = \frac{R_a - R_g}{R_a} \times 100\%$$

where R_a is resistance of pellet in air and R_g is the resistance of pallet in presence of gas under study.

3. Results and discusion

3.1. X-ray diffraction analysis

The x-ray diffraction patterns (XRD) of pure and Pd-doped SnO_2 samples for different concentrations were investigated with x-ray diffractometer. The observed pattern has a number of sharp peaks at (110), (101), (200), (211), (002), (310) and (112) at different angles