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Effect of hydrolysis ratio on structural, optical and electrical properties of SnO_2 nanoparticles synthesized by polyol method

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ABSTRACT

Using the polyol method and a thermal post-treatment, nanoporous tin dioxide (SnO_2) were prepared at different hydrolysis ratio (h = n (H_2O)/n (Sn)). The influence of the hydrolysis ratio on the structural, textural, optical and electrical properties of SnO_2 nanopowders was investigated by employing a set of various techniques including Fourier Transform Infra-Red spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), Energy Dispersive X-ray spectroscopy (EDX), Scanning Electron Microscopy (SEM), Nitrogen Sorption Porosimetry and Impedance Spectroscopy. FTIR and EDX studies revealed that SnO_2 species were obtained. Nanocrystallites of cassiterite, i.e. rutile-like tetragonal SnO_2 structure, were formed after annealing in air at 700 °C and the average crystallite size increased from 12.8 to 29.1 when the hydrolysis ratio rose from 17 to 24. Moreover, TEM, SEM, and N_2 sorption porosimetry investigations indicated that the sample prepared for h = 17 was composed of an aggregated network of almost spherical nanoparticles, the morphology and sizes of which changed with the increase in the hydrolysis ratio to h = 24 and the mesoporosity of which was found to be linked to the interparticle space. Moreover, this increase in mean nanoparticle size was accompanied by a decrease in the band gap value from 3.4 eV (h = 17) to 3.16 eV (h = 24). Finally, bulk conductivity dependence with temperature was found to follow an Arrhenius law for samples annealed at 700 °C with an activation energy of 0.65 eV for h = 17, 0.69 eV for h = 20 and 0.71 eV for h = 24 that is typical of SnO_2 nanopowders.

1. Introduction

Shape, size, and dimensionality are essential parameters ruling the properties of metal oxide semiconductors and, as a consequence, developing an easy process to prepare metal oxide nanomaterials with clearly-defined structures is of vast interest and importance. In particular, crystalline tin dioxide (SnO_2), cassiterite structure, is a wide band gap semiconductor (~3.6 eV), which, in its as-grown state, is typically n-type which find widespread applications because of its optical (transparent for visible light and reflective for Infrared (IR)) and electrical properties, combined with high chemical and mechanical stabilities. Properties of SnO_2 nanomaterials depend on microstructure, impurities, and size effects of particles. Thus, nanostructured SnO_2 particles have been synthesized using different chemical methods such as hydrothermal methods [1,2], chemical vapor deposition (CVD) [3], thermal evaporation [4], co-precipitation [5] and polyol procedures [6–8]. Among these various routes, the polyol method is well suited for the production of nanostructured materials, because of its relatively low processing cost and its ability to control the grain size. A key advantage of polyol process-based nanoparticle synthesis is that the kinetics of the reaction can be readily controlled, as established by Fievet et al. [9,10]. Furthermore, SnO_2-based nanomaterials have been widely studied for applications in photocatalysis to decompose undesirable organic matters [11,12], optoelectronic devices [13], transistors [14,15], lithium ion batteries

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[16,17], supercapacitors [18,19], dye-sensitized solar cells [20,21], and gas sensors [22,23]. The sensitization of wide gap semiconductors such as TiO_2 and ZnO [24] has gained significant attention owing to their high photostability. Furthermore the composite photocatalysts such as ZnO/SnO_2 [25,26], tin-doped TiO_2 [27] and SnO_2/TiO_2 [28,29] have been widely researched [30,31] for their high photocatalytic activities. However, to date only a few studies have been conducted to investigate SnO_2 [32–34].

In this context, we herein report on an easy polyol method to synthesize uniform SnO_2 spherical nanoparticles with adjustable size based on the tuning of the hydrolysis ratio h defined as n(H_2O)/n(Sn). The resulting nanostructured SnO_2 powders were characterized by various techniques such as FTIR, XRD, UV–visible spectroscopy, N_2 sorption, SEM and TEM. The influence of the hydrolysis ratio on the properties of SnO_2 nanoparticles (crystal structure, grain size, specific surface area, and average pore size) was carefully investigated. Finally, the electrical properties of the best crystallized samples were determined by impedance measurements.

2. Experimental

2.1. Synthesis of SnO_2 nanoparticles

SnO_2 powders were prepared by the polyol method. In a typical experiment, 6.57 g of tin (IV) tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98%, Aldrich) were dissolved in 50 ml of Diethylene Glycol (DEG, 99%, Aldrich) and 10.20 g of sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$, 99%, Scharlau) in 75 ml of DEG. After introducing the tin tetrachloride solution in a three-necked flask, an appropriate volume of demineralized water was added to adjust the hydrolysis ratio h (for instance, taking into account the water molecules provided by the precursors used, 1.1 mL to reach h = 20 and 2.36 mL to reach h = 24) and the resulting solution was heated up to 120 °C. The sodium acetate solution was then added dropwise using a dropping funnel. Then the temperature was raised to 160 °C in order to initiate the precipitation of SnO_2. The reaction medium was further heated at 160 °C for 7 h. After cooling to room temperature, the obtained SnO_2 powders were washed several times with water and ethanol, and isolated by centrifugation. Drying at 90 °C overnight followed by calcination in air at 700 °C for 8 h gave 3 g of a white powder [35].

2.2. Characterization

Optical absorbance in the UV–visible range of the SnO_2 nanoparticles was analyzed using Shimadzu UV-3101 PC spectrophotometer equipped with an integrating sphere in the 200–2000 nm wavelength range. FTIR spectra (KBr pellets) were recorded by means of Thermo Nicolet 670 Nexus spectrophotometer (FTIR) spectrometer. X-ray diffraction studies were carried out with Bruker AXS Advance diffractometer (D2 PHASER A26-X1-A2B0D3A) equipped with a source delivering a monochromatic Cu anode (Kα radiation, λ = 1.54056 Å). The θ-2θ scans were recorded in an angular range between 10 and 80° with a step of 0.02°. Specific surface areas (Brunauer-Emmett-Teller (BET)) of SnO_2 nanoparticles were deduced from N_2 sorption analyzes performed with a Micromeritics ASAP2010 equipment. TEM images were recorded on a JEOL JEM-2100 microscope and elemental analyses were performed with a EDS (Energy dispersive X-ray spectroscopy) system (Oxford, Wiesbaden, Germany) connected to the JEOL JEM-2100 microscope. The electrical properties of the SnO_2 nanoparticles calcined at 700 °C were determined using impedance spectroscopy (IS) technique. The latter is indeed a powerful tool to characterize many of the electrical properties of materials and their interfaces. In our case, the polycrystalline sample was pressed into pellets of 8 mm diameter and 1.2 mm thickness using 3 t/cm^2 uniaxial pressures. Electrical impedances were measured in the frequency range from 200 Hz to 5 MHz with TEGAM 3550 Alfred automatic bridge and in the temperature range between 598 and 733 K. The variation of both real (Z′) and imaginary (Z″) parts of the complex impedance ($Z^* = Z' - iZ''$) were investigated.

3. Results and discussions

3.1. FT-IR studies

The FTIR spectra of SnO_2 nanoparticles calcined at 700 °C at different hydrolysis ratio (h = 17, 20 and 24), defined as the ratio of the amount of water by the total amount of metal (n(H_2O)/n(Sn)) (including the quantity of water present in the precursor salts), are quite similar as depicted in Fig. 1. The broad absorption peak observed between 3250 and 3600 cm^{-1}, was due to the fundamental stretching vibrations of hydroxyl groups (free or bonded) which were further confirmed by weak band at about 1630 cm^{-1} attributed to the bending vibration of coordinated H_2O as well as Sn-OH [35,36]. The broad absorption band centered at 619 cm^{-1} can be assigned to the stretching vibration of Sn-O bond in SnO_2 lattice. The peak around 1048 cm^{-1} is ascribed to the (ν(C–O)) vibrations [35], while the band located at 1360 cm^{-1} is owing to the bending vibration of –CH_2, which shows that a few organic groups are absorbed on the surface of SnO_2 due to the DEG (Fig. 1, black) [37,38].

3.2. Structural studies

Fig. 2 shows the XRD patterns of SnO_2 samples at different hydrolysis ratios ((h = 17, 20 and 24). All the diffraction peaks in the pattern corresponded to the tetragonal rutile structure of the polycrystalline SnO_2 in good agreement with the reported data (JCPDS file No. 41-1445) [39]. No other diffraction peaks corresponding to other SnO_2 polymorph or any crystalline impurity was detected, indicating that the product contains only the cassiterite polymorph with a good crystallinity.

However, the comparison of the diffraction patterns of the samples prepared using a hydrolysis ratio of 17, 20 and 24 revealed a variation in both intensity and broadness of the peaks. The peaks

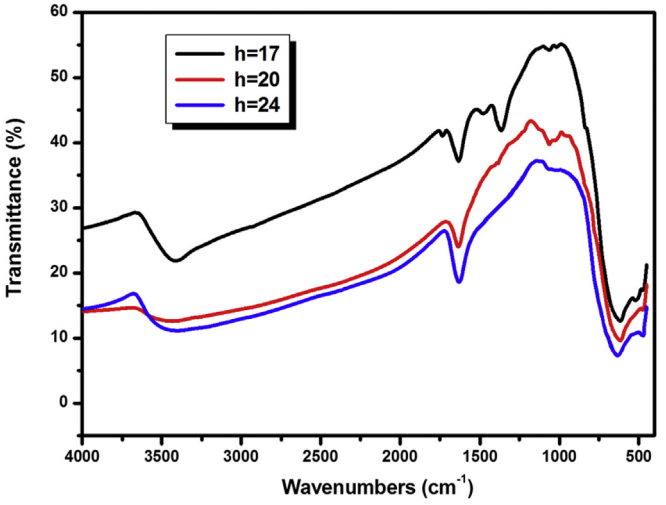

Fig. 1. FTIR spectra of SnO_2 nanoparticles synthesized for hydrolysis ratio h = 17 (black), h = 20 (red) and h = 24 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)