Journal of Alloys and Compounds 547 (2013) 11–17

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Hygrophila spinosa T. Anders seeds based biomineral doped cobalt oxide: Synthesis, characterization and its application to humidity sensing

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ARTICLE INFO

Article history:
Received 16 March 2012
Received in revised form 14 August 2012
Accepted 16 August 2012
Available online 3 September 2012

Keywords:
Hygrophila spinosa T. Anders
Co_3O_4
Humidity sensor
Mixed metal oxide
Biominerals
Sensitivity factor

ABSTRACT

Hygrophila spinosa T. Anders plant seeds (HST) possessing gelling behavior with mineral constituents have been chosen as a dopant in cobalt oxide (Co_3O_4) to investigate the humidity sensing properties. The study on the structural parameters, functional groups, BET surface area, surface morphology and elemental analysis of the prepared sensor samples was made using XRD, FT-IR, nitrogen adsorption/desorption isotherms at 77 K, SEM and EDX techniques respectively. The humidity sensitivity factor (S_f) of the prepared samples was evaluated by two probe dc-electrical resistance method at different humidity levels. The S_f value determined suggested that the sample with the weight ratio of Co_3O_4:HST biominerals of 0.25:0.75 respectively was beneficial for increasing the sensitivity factor possessed relatively a higher value, i.e. 4500. Good linearity, reproducibility, stability and fast response time (5.5 ± 0.25 min) and recovery time (2.5 ± 0.08 min) achieved in CH3 sample is indicative to be a good humidity sensor.

1. Introduction

Humidity is the most important environment parameter to monitor and control, since it directly affects the various industrial processes like, end product quality, the functionality of equipment and quality control process [1]. Therefore, the humidity sensing devices plays an vital role to measure the humidity and finds its widespread applications in various sectors like, agriculture, medicine, textiles, storage of food stuffs, domestic applications, cooling, human comfort, industrial processes, etc. [2,3]. Various materials like polymers, metal oxide based ceramics and composites [4,5] are used widely as humidity sensor, by detecting changes in their capacitance or resistance. Although, polymer sensor provides good mechanical properties, ease of processing, etc., they show poor response, low accuracy at high humidity and stability. To overcome its demerits, the combinations of metal oxide based semiconducting ceramics are preferred due to their notable change in electrical resistance and the surface chemistry. In addition, metal oxides are more advantageous compared to others, for its high stability, wider operating temperature, rapid response and recovery time [6]. In general, cobalt oxide exists in three different crystalline forms namely, CoO, Co_2O_3 and Co_3O_4. Among all stoichiometry, Co_3O_4, is used for various application due to its chemical stability and desired electrochemical properties [7]. As a basis of functional materials, Co_3O_4 have been extensively employed in, high temperature solar selective absorbers, electrochemical capacitors, optical gas sensors, optical humidity sensors, heterogeneous catalysts in oxidation process, magnetic materials and lithium-ion battery electrodes [8–15]. However, to the best of our knowledge, there are only very few literature available on the humidity sensing properties of Co_3O_4 in which they are measured by optical methods [1,16,17]. Cobalt oxide nanosheet humidity sensor integrated with circuit on chip was also reported [15]. But, there is no report available in literature regarding Co_3O_4 humidity sensor through electrical conductivity studies.

In our work, the synthesized pristine Co_3O_4 shows poor sensing performance towards humidity, as the resistance values do not abruptly change at higher relative humidity (RH) values resulting in low values of humidity sensitivity factor. Aiming to increase the sensitivity and selectivity, studies have shown that surface chemistry, dopant type and preparation conditions are the most important factors. Hence, we focused our present work to dope mineral oxides derived from bioresources. For this purpose, the seeds of *Hygrophila spinosa* T. Anders, a well known medicinal plant, rich in mineral content and found abundantly in the paddy fields and marsh areas, are used. This plant is widely distributed throughout India, Sri Lanka, Burma, Malaysia and Nepal [18]. The roots, leaves and seeds of this plant find a prominent place in Ayurveda and Unani medicines. The seeds of *H. spinosa* T. Anders

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http://dx.doi.org/10.1016/j.jallcom.2012.08.094

contain minerals like Ca, Mg, K, Fe, Cu, etc. [19]. Hitherto, no research work has been undertaken to explore the possible effects of the addition of mineral contents of *H. spinosa* T. Anders onto Co_3O_4 towards gas or humidity sensitivity detection. Hence, the main intention of the present work is to study the effect of humidity sensing on Co_3O_4 by the addition of *H. spinosa* T. Anders seeds. The prepared humidity sensor was extensively characterized by thermogravimetric analysis, X-ray diffraction, FT-IR spectroscopy, scanning electron microscopy and energy dispersive X-ray analysis, surface area, porosity. The sensitivity of the samples was calculated by exposing the samples to different relative humidity levels, ranging from 5% to 98% as a function of change in the resistance values. The other parameters such as stability, response and recovery time are also evaluated.

2. Experimental details

2.1. Materials

Analytical grade $Co(NO_3)_2{\cdot}6H_2O$ and poly vinyl alcohol (PVA) were purchased from SD fine chemicals, India. Deep brown colored *H. spinosa* T. Anders seeds (HST) that were approximately 2 mm diameter in size were obtained from the local ayurvedic medical store located at Chennai, Tamil Nadu, India.

2.2. Preparation of HST doped Co_2O_3

The weight ratios of Co_3O_4:HST chosen were 1.0:0.0, 0.75:0.25, 0.5:0.5, 0.25:0.75 and 0.0:1.0 and were labeled as CH0, CH1, CH2, CH3 and HS respectively. Prior to preparation, the HST seeds were cleaned well to remove the dust, and subjected to dry-grinding. The ground HST of an appropriate weight was taken in a separated beaker and distilled water was added to it slowly under continuous stirring. During the continuous stirring, HST turned a gelly substance and settled at the bottom of the beaker. After settling, the excess water was drained out and the gel was washed several times in the distilled water until the water after wash was very clear. The after-wash water was again drained out completely. $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water in a separate beaker and was added to HST gel kept in another beaker and stirred thoroughly for about 5 h to form a uniform gelly mixture. This HST–$Co(NO_3)_2{\cdot}6H_2O$ gelly mixture was kept in hot air oven at 110 °C overnight, which resulted in a dark brown dry substance. It was later calcined at 600 °C for 5 h at the heating rate of 5 °C/min, in order to bring about a thermal decomposition, phase transition and removal of certain volatile components present in the HST and metal salts mixtures. The mixtures were converted into metal oxides. The calcined samples were then wet milled and dry milled for 4 h respectively and thick pellets of 13 mm in diameter were made, using PVA as the binder in a hydraulic press. Finally, the pellets were sintered at 900 °C for 5 h at a heating rate of 5 °C/min in a microprocessor controlled furnace, to promote doping effect, growth of grain size and bring the powder particles together to create one uniform solid matrix. The sintering temperature of 900 °C was fixed from the thermogravimetric analysis curve shown in Fig. 1. The curve showed the sudden loss of weight between 100 °C and 450 °C in HST due to dehydration and decomposition of water molecules and low volatile constituents like sterols and alkaloids. The calculated weight loss around 15.12% within the temperature range of 450–900 °C is due to the release of tightly bound lignocellulose volatile components, which was not released at lower temperature. Since the thermal stability was attained around 900 °C, all the HST doped samples were opted to be sintered at 900 °C. The sintered pellets were labeled accordingly, based on the weight ratios taken as mentioned earlier. In the present study, the *H. spinosa* T. Anders seeds are labeled as HST, while the sintered pristine HST seeds are labeled as HS.

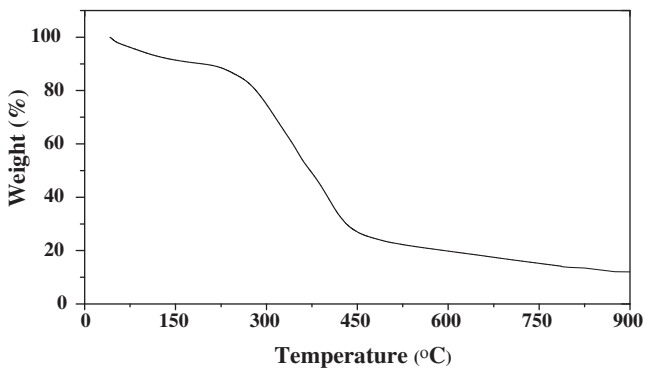

Fig. 1. Thermogravimetric analysis of *Hygrophila spinosa* T. Anders (HST).

2.3. Characterization

The structural phases were determined by powder X-ray diffraction (XRD) technique, recorded in a Philips X'pert diffractometer for 2θ values ranging from 5° to 80°, using Cu Kα radiation at $\lambda = 0.154$ nm. The FT-IR (Fourier Transformer-Infra Red) spectra of the samples were recorded, using a Perkin–Elmer Infrared spectrometer to detect the vibration stretching frequencies. The samples were scanned in the spectral range of 4000–400 cm^{-1}. The surface morphology of the samples was determined using high resolution scanning electron microscope (HRSEM) at the desired magnification. The energy dispersive X-ray analysis (EDX) was measured, using Oxford Instruments, Eynsham Oxford, England at 15 kV. Nitrogen adsorption/desorption isotherms of the sample were carried out at 77 K using Quantasorb I analyzer to determine the BET surface area, pore size and pore volume using Brunner–Emmett–Teller (BET) equation. Thermogravimetric analysis (TGA) was performed using SDT Q 600 to determine the weight loss from the room temperature to 900 °C under N_2 atmosphere.

2.4. Humidity measurements

The dc electrical resistance at different relative humidity levels of the samples in the form of pellets was determined by a two-probe method, instead of the Van der Pauw four-probe method, as the present work is to measure the changes in surface conductivity from the function of applied field and the current. Conducting silver paste was employed to ensure the ohmic contacts. The samples were electrically connected to a dc power supply and a Keithley 614 electrometer in series. Given the high resistivity of the materials under investigation, the potential inaccuracy due to contact resistance is assumed as negligible. The controlled humidity environments were achieved using anhydrous P_2O_5 and saturated aqueous solutions of $CaCl_2{\cdot}6H_2O$, $Ba(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $NaNO_2$, NH_4Cl, $BaCl_2{\cdot}2H_2O$ and $CuSO_4{\cdot}5H_2O$ in a closed glass vessel at an ambient temperature of 298 K, which yielded approximately 5%, 31%, 42%, 51%, 66%, 79%, 88% and 98% relative humidity (RH), respectively, and that was also exactly measured with a Barigometer [20,21]. Heat cleaning of the samples was found to be a must for a better sensitivity. Hence, the sample was heated to 373 K, followed by cooling in a humidity-free atmosphere before and after the sensitivity measurements, especially when the sensors were operated at high RH. The samples were exposed to the respective RH% until the saturation is reached around 1 h. The sensitivity factor (S_f) was calculated by the ratio of resistances, $R_{5\%}/R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ were the dc resistances, at 5% and 98% RH, respectively. A degassed glass chamber (200 cm^3) was used for the evaluation of response and recovery characteristics. This chamber has got a provision for a two-way inlet, one for transpiring dry air from 5% RH and the other for transpiring moist air containing 98% RH. The response and recovery characteristics were studied between 5% and 98% RH conditions. The resistance measurements in dry air as well as in moist air alternatively helped to establish the recovery and response characteristics for moisture sensing.

3. Material characterizations

3.1. X-ray diffraction studies

The XRD patterns of pristine Co_3O_4, HST doped Co_3O_4 samples and HS are shown in Fig. 2a–e. All the diffraction peaks for the samples match with the face-centered cubic system of the spinel structure of Co_3O_4 (JCPDS: 76-1802) except HS sample (Fig. 2e). It is quite clear from the XRD spectra that the diffraction peaks are sharp indicating highly crystalline behavior. The crystallite size was calculated, using the Scherer formula all the samples are shown in Table 1. The HST doping 25% (3%), 50% (6%) and 75% (9%) in samples CH1, CH2 and CH3 respectively are well evidenced by the reduction in intensity of the XRD peaks due to the strains produced in the crystal lattice [22]. The values in the bracket indicate the percentage of mineral content present in HST for the respective weight percentage for a particular composition. The XRD pattern of HS (Fig. 2e) shows numerous diffraction peaks attributed to the presence of prominent mineral contents like Si, Mg, Al and K as evidenced from the EDX spectra (Fig. 3c). However, the indexing of the diffraction peaks in HST was found difficult as it is taken from bio-resources [23]. Fig. 3b shows the presence of peaks due to HS in addition to the normal peaks available for