Structural Characterization of NiO/Cr_2O_3Composites and Hydrothermal Synthesis, Properties Gas Sensing

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Abstract

Pure Cr_2O_3 and NiO/Cr_2O_3 nanocomposite were luckily synthesized by simple hydrothermal technique. X-ray films diffraction (XRD), Filed Emission scanning electron microscopy (FESEM), Energy dispersive X-ray spectroscopy (EDS), were used to research the crystalline structures, surface morphologies and nanostructures, and element components and their valences of the as-synthesized samples. Moreover, gas sensors based on the synthesized pure Cr_2O_3 and NiO/ Cr_2O_3 composites were fabricated and their sensing behavior, to NH_3.Gas sensing experiments reference that the NiO/ Cr_2O_3 composites showed much higher gas response and lower working temperature than those of pure Cr_2O_3. These results assure that the as-synthesized NiO/ Cr_2O_3 composites a favorable NH_3 sensing material. [DOI: 10.22401/JUNS.21.1.10]

Keywords: nanocomposite, chromic oxide, nickel oxide, hydrothermal method.

1. Introduction

In the recent years, the various size and shape of different nonmaterial has been realized through a wet-chemical synthesis because of its wide range of application. Owing to this reason researchers showing an increasing interest to fabricate nanostructured materials [1]. In this present work we prepared nano particles and nanocomposites using wet-chemical synthesis [2]. Its applications are extended by changing its physical and chemical properties under nanoscale due to large range of surface to volume ratio [3]. In spite of unusual structural geometry, semiconductor metal oxide nanostructures are of great interest of research in nanoscience and nanotechnology, because of the fact that this class of compound is frequently revealing the novel properties relative to their coarse-grained counterparts, due to their reduced size and large surface area [4]. The chosen metal oxide nanoparticles like chromic oxide and nickel oxide is an important transition metal oxide of p-type semiconducting materials with a band gap of 3 eV and 3.8 eV. These metal oxide nanoparticles and metal oxide nano composites were used as a gas sensors, electro chromic films and fuel cells etc. Generally nanocrystalline metal oxides and metal oxide nanocomposites have been prepared by wet-chemical techniques such as sol-gel, solvothermal and co-precipitation methods etc. Metal oxide gas sensors have been widely used in portable gas detection systems because of their advantages such as low cost, easy production, compact size and simple measuring electronics. However, the performance of such sensors is significantly influenced by the morphology and structure of sensing materials, resulting in a great obstacle for gas sensors based on bulk materials or dense films to achieve highly-sensitive properties [5,6]. In the present communication, we report the deposition of nanocrystalline NiO/ Cr_2O_3 films by print screen method at low temperature and gas response properties.

2. Experimental

A. Preparation of Pure Cr_2O_3 and NiO/Cr_2O_3 Composites. The sensing materials in this research, that is, pure Cr_2O_3 and NiO/ Cr_2O_3 composites, were synthesized with a simple, facile, and hydrothermal method. In a typical synthesis process, 0.1M Cr $(NO_3)_3.9H_2O$ and 0.1M Ni $(NO_3)_2{\cdot}6H_2O$, 0.3M ammonium carbonate $((NH_4)_2CO_3)$,1g of $(C_6H_8O_7)$, 30ml absolute ethanol, and 30ml distilled water were mixed both with strong magnetic stirring in a 100ml capacity beaker. Then the mixed solution was transferred into a 100ml Teflon autoclave, the autoclave was sealed and maintained at 180^{O}C for 24 h [7],

and then allowed to cool to room temperature naturally. After terminating the reaction in desired time, the resulted solid projects, washed with distilled water and ethanol to remove the ions possibly remaining in the final product, and dried in air at 80°C for 24 h. Finally, the prepared powder will be undergone to calcination process for 2 hour at 400 °C.

B. Preparation of Thick Films

The films were prepared using hydrometallic technique for each nanopartical and nanocomposite .The thixotropic paste was formulated by mixing the fine powder of as prepared with the solution of (a temporary binder) in a mixture of organic solvents such as ethyl acetate. The ratio of inorganic part to organic part was kept at 70:30 in formulating the paste. This thixotropic paste was used to deposit thick films on ultrasonically cleaned silicon substrate (2cm x 1cm) was used [8]. The films were fired at 550°C for 30 min.

3. Characterization

Structural characterization of Pure Cr_2O_3 and NiO/ Cr_2O_3 nanocomposites. The structures crystalline of the samples prepared were completed by X-ray films diffraction (XRD) 40 kV and 30 mA with monochromatic CuKα radiation (λ=1.54056 Å) and the scanning 2θ range from 20 to 70º, field emission scanning electron microscopy **(**FE-SEM), Energy dispersive X-ray analysis (EDX) was used to estimate the composition of the materials and optical properties. Properties of gas sensor the fabricated sensors to NH_3. The gas response account of the sensor was specified as the ratio of sensor resistance in air to that in a mixture of NH_3 gas and air. The response and recovery times were defined as the time possessed through the sensor.

3. Results and Discussion

3.1. XRD

Fig.(1) shows the XRD pattern of the pure Cr_2O_3 nanoparticles prepared using hydrothermal method. The XRD peaks (012) (104), (110), (113), (024), and (116) peaks by comparing with the (JCPDS file no. 38–1479), which clearly indicates Cr_2O_3 nanoparticles are of rhombohedral phase. From the XRD peaks, the Cr_2O_3 average crystallite size of particles was calculated from Debye Scherer formula [9]:

$$D = 0.9\lambda / (\beta \cos\theta) \quad \text{.....(1)}$$

Where λ is the wavelength of X-rays used (1.5405Å), β is the Full Width Half Maximum (FWHM) in radian and θ is the angle of diffraction. The calculated average crystallite size from the XRD peaks for pure Cr_2O_3 nanoparticles was found to be 25nm. The XRD pattern of NiO/Cr_2O_3 nanocomposites synthesized by hydrothermal method. The XRD peaks (111), (110), (200) and (214) were confirming the formation of NiO/ Cr_2O_3 nanocomposite. The peaks are coinciding with which shows the crystal structure of Cr_2O_3 belonging to rhombohedral phase, and the weak peaks like (113) and (220) matching with the (JCPDS file no. 38–1479) shows the crystal structure of NiO belonging to the cubic system. The XRD analysis reveals that the prepared nanocomposite has composed of cubic NiO and rhombohedral Cr_2O_3. From the XRD pattern, the average crystallite size of NiO/ Cr_2O_3 nanocomposites was calculated from Debye Scherer Formula and its value was calculated as 9.7 nm [10].

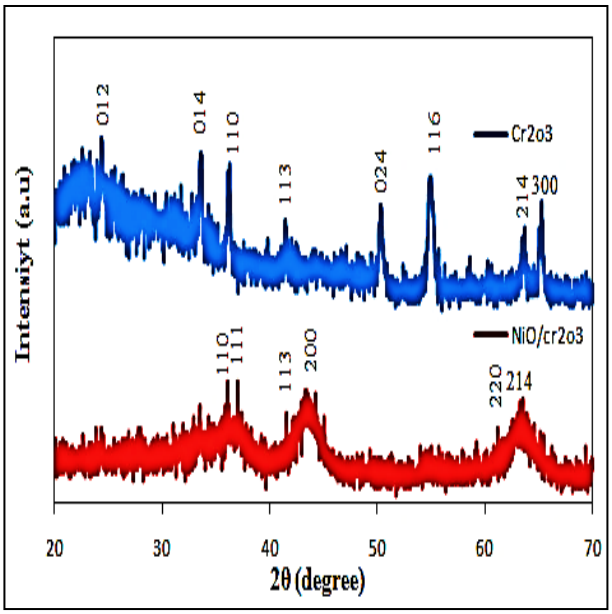


Fig.(1): XRD patterns of pure $Cr_2O_3$and NiO/ Cr_2O_3 nanocomposite.

3.2 Morphology Analysis of NiO/ Cr_2O_3 nancomposites

Energy dispersive X-ray spectroscopy measurement was completed to make express the element components of the as synthesized samples and test, whether Ni element has been luckily into the synthesized Cr_2O_3 nanoparticals. Fig.(2) shows the EDS spectrum of NiO/Cr_2O_3 composites NPs, it shows the presence of Cr, Ni and O peaks confirming the formation of both NiO and Cr_2O_3.

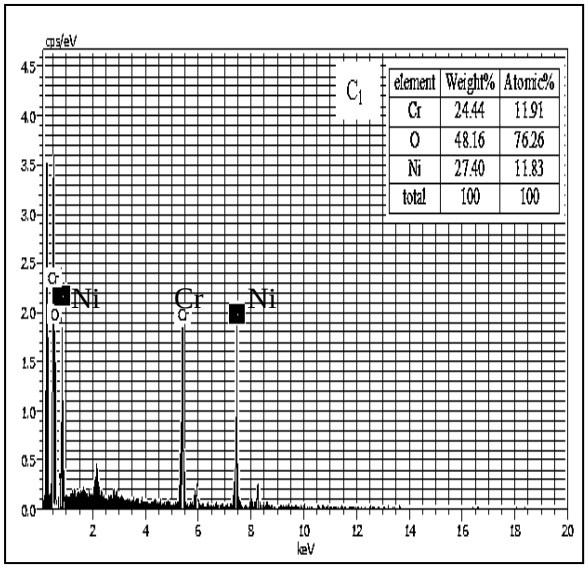


Fig.(2): EDX analysis of NiO/ Cr_2O_3 nanocomposite.

The size and morphology for the NiO/ Cr_2O_3 nanocomposites was characterized using FESEM studies. The surface structure and morphology characteristics of the as-prepared samples were completed by FESEM and shown in Fig.(3). As shown in Fig.(3) it can be seen that the pure Cr_2O_3 and NiO/Cr_2O_3 composites nanostructures nanoparticals were nearly uniform spherical shapes and very small particles in evidently dispersed without large agglomerates. The diameters of pure Cr_2O_3 nanoparticals from 30 to 60 nm and from 20 to 30nm for NiO/Cr_2O_3 samples. These results indicate that in this study NiO dopant only has a slight influence on the structures and morphologies of pure Cr_2O_3 nanostructures except for an evidently inhibitory effect on its crystalline growth.

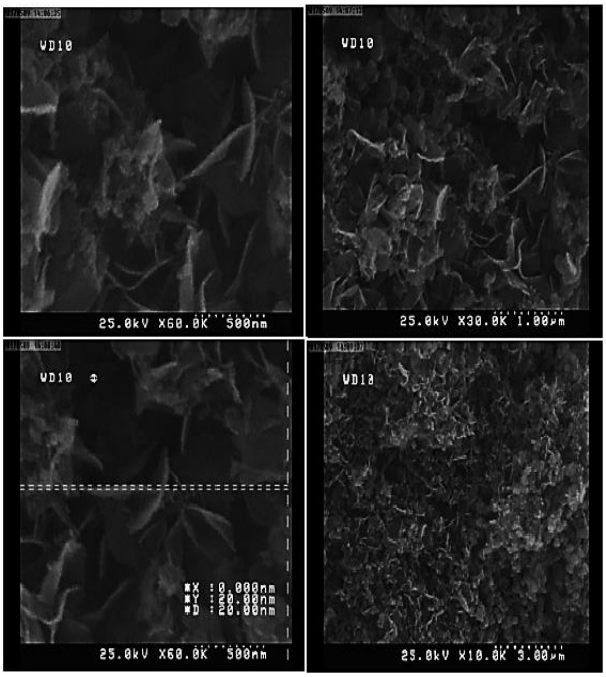


Fig.(3): FESEM image of NiO/ Cr_2O_3 nanocomposite.

3.3. Optical Properties

UV-vis absorption spectroscopy was used to inset agate the optical properties at room temperature, optical absorption spectra for pure Cr_2O_3 and NiO/ Cr_2O_3 nano composites are shown in Fig.(4). The spectra show a strong absorption below 550nm. The optical band gap energy (E_g) of the as-synthesized nanoparticles is obtained from the UV-Vis spectra by using a well-known Tauc's relation [11]:

$$(\alpha h\upsilon) = A\,(h\upsilon - E_g)^n \quad \text{.....(2)}$$

where, α is the absorption coefficient, A is a constant, E_g is the bandgap energy of the material and exponent n = ½ for direct transition.

This absorption spectrum of chosen nanocomposite material band gap obtains value of Cr_2O_3 and NiO/ Cr_2O_3 2.9 and 2.7eV [12]. This may be attributed due to the charge transfer between the nanocomposite materials [9]. From the UV analysis we came to the conclusion that the band gap of a material increases when particle size of nanocomposites decreases [13].

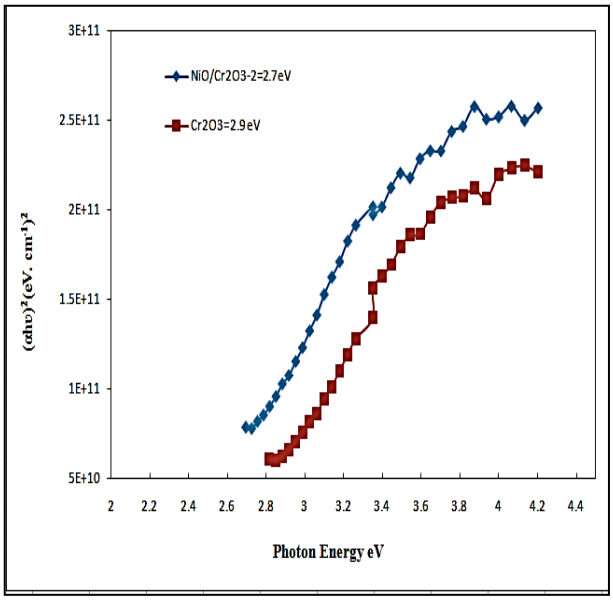


Fig.(4): The energy gap for NiO/ Cr_2O_3 nanocomposite.

3.4. Gas Sensing Properties

Firstly, the sensors fabricated from the synthesized pure Cr_2O_3 and NiO/Cr_2O_3 composites were exposed to a certain concentration of NH_3 gas at various working conditions to find out the optimum operating temperature. Fig.(5) shows the gas responses of the prepared sensors for gas NH_3 the operating temperature from 35 to 300^oC.

For all sensors, its gas response increases quickly initially and obtain its maximum gas response value and then decreases rapidly with increasing temperature. As shown in Fig.(5) the operating temperature of NiO/Cr_2O_3 composites was submit to be 100^oC for pure Cr_2O_3 samples, where the sensor display the maximum gas response value at this status. Simultaneously, at the optimum working status, the symmetric NH_3 gas response is 76% at 200^oC for NiO/ Cr_2O_3composites and 22.12 at 100^oC for pure Cr_2O_3 samples. The catalytic nature and lower ionization energy of chromium as compared to zinc caused reduction of activation energy of the reaction between target gas molecules and surface adsorbed oxygen which leads to fall in operating temperature of zinc oxide gas sensor. The low is the ionization energy, the less is energy required to knock out electron which leads to reduction in activation energy of chemisorption of gases [14]. The lowering of activation energy due to catalytic effect can take place by two possible mechanisms. First, it can concentrate the reactants by adsorption, thus increasing their probability of interacting. Second, it can introduce a reaction route of very low activation energy.

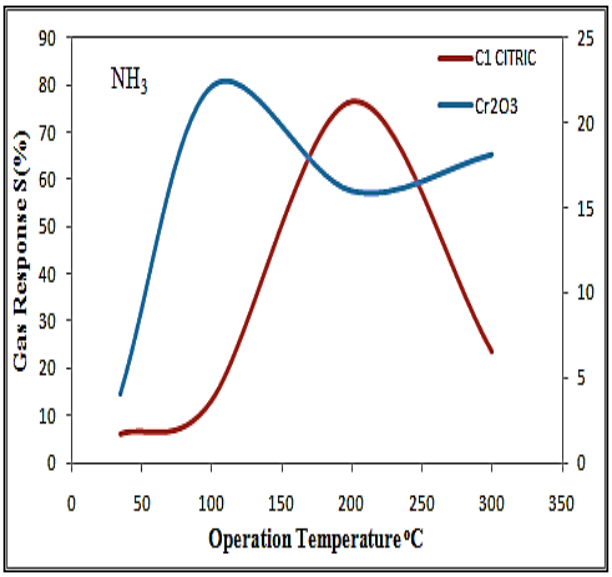
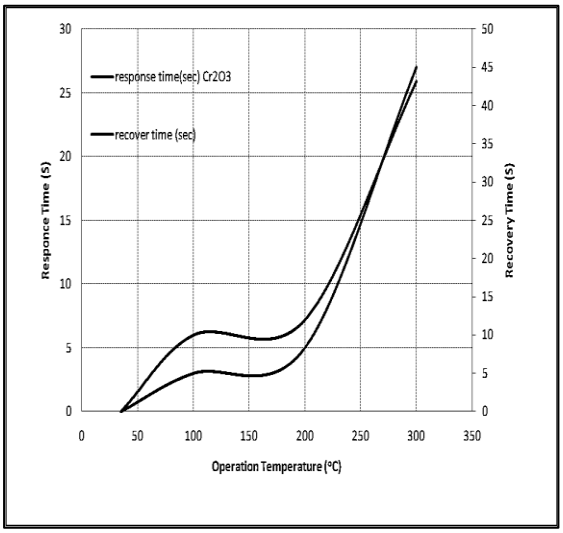


Fig.(5): Sensor response as a function of operating temperature at working from35 to 300^oC of NH_3.

It is well known that response and recovery characteristics are important for evaluating the performances of semiconductor oxide sensors. Fig.(6) shows the response and recovery properties of the Cr_2O_3 and NiO/ Cr_2O_3 composites sensors of NH_3 gas at operating temperature. It can be seen in Fig.(6) that compared with Cr_2O_3 and NiO/Cr_2O_3 composites, the sensor based shows shortest response and recovery time (12s and 47s, resp.). Such a rapid response and recovery property could be attributed to the excellent electronic sensitization and catalytic activities.



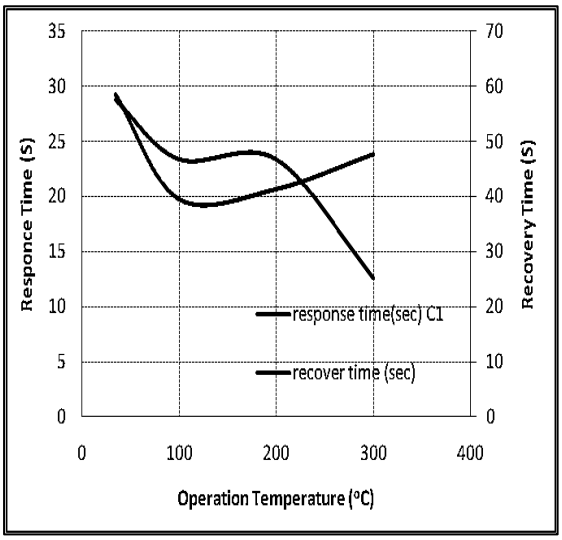


Fig.(6): Response time of Cr_2O_3 and NiO / Cr_2O_3 nanocomposite sensor for NH_3.

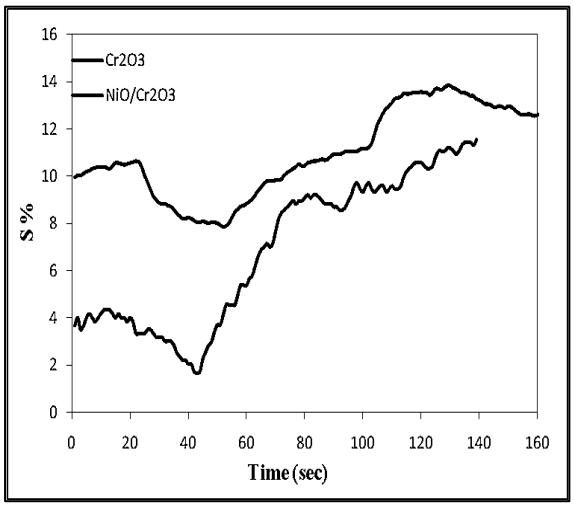


Fig.(7): Plots of dynamic response for Cr_2O_3 and NiO/ Cr_2O_3 nanocomposite of NH_3.

4. Conclusion

Cr_2O_3 and NiO/ Cr_2O_3 composite film sensors were synthesized by using hydrothermal and screen printing routes. XRD studies confirmed the formation of NiO/ Cr_2O_3 composite materials having crystallite sizes of Cr_2O_3 25 nm and NiO/ Cr_2O_3 9.7nm . EDX analysis corroborated the presence of the Ni,Cr and O in the samples. The gas sensing results showed that gas NH_3 response is 76% at 200^oC for NiO/ Cr_2O_3composites and 22.12 at 100^oC for pure Cr_2O_3 samples with fast response (12 s) and recovery time (47 s). The enhanced response was attributed to the smaller crystallite size, which helped in greater oxygen adsorption on the film surface.

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