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Green synthesis of $CdFe_2O_4$ nanoparticles and their application for ethanol vapor sensing

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The work reported about preparation of nanocrystalline $CdFe_2O_4$ through an combustion method and characterization of their microstructural, morphological and gas sensing properties. The structural properties investigated by X-ray diffraction revealed with $CdFe_2O_4$ cubic structure. crystallite size was found to be ~ 64 nm. The morphological study characterized by scanning electron microscopy and transmission electron microscopy. The sensor fabricated from these nanocrystalline $CdFe_2O_4$ exhibits high sensitivity and rapid response/recovery to ethanol at 350 °C. The sensitivity was up to 59.23% when the sensor was exposed to 50 to 200 ppm ethanol and the response and recovery time is about 40 and 50 s respectively. The linear dependence of sensitivity on the ethanol concentration was found in the range 50-200 ppm. Hence studies revealled that nanocrystalline $CdFe_2O_4$ can be used as sensing material for fabricating high performance ethanol sensors.

Keywords: $CdFe_2O_4$, Ethanol, Thick film, Nanocrystalline, Sensors.

Introduction : Design and fabrication of chemical sensors has become one of the most active research fields due to their wide applications in many fields, such as industrial production, process control, environmental monitoring, healthcare, defence and security [1 - 4]. Due to potential applications of nanomaterials, several new synthesis routes [5 - 8] for the production of nanocrystals with desired properties have been developed. Transition metal oxides (MFe_2O_4) are nano materials with cubic spinel structure which have been extensively used in various technological applications in the past decades, spinel-type oxides with a general formula of AB_2O_4 have attracted considerable attention because of their promising applications in gas sensors [9 - 12]. The gas-sensing mechanism of metal oxide materials is based on the reaction between the adsorbed oxygen on the surface of the materials and the gas molecules to be detected. The state and the amount of oxygen on the surface of materials are strongly dependent on the microstructure of the materials, namely, specific area, particle size, as well as the film thickness of the sensing film. In order to obtain gas sensors with good performance, the recent research works were devoted to nano-materials because they have high specific area and contain more grain boundaries. Recently, inspired by the advantages of small size, high density of surface sites and increased surface to volume ratios, synthesis of these semiconductor metal oxides with nanostructures and exploration of their properties are of current interest their excellent sensing performances are based on the nanopowder that may great influence on their chemical and physical characteristics [13].

In this paper, we present a simple and effective route for the synthesis of $CdFe_2O_4$ nanopowder with excellent ethanol sensing properties. The sensor fabricated from these nanopowder exhibits high sensitivity to ethanol vapour and the response and recovery time is about 40 s and 50 s, respectively. These high sensing performances are based on the spinel structure of the nanopowder.

Experimental :

Preparation of materials : For the present study, polycrystalline $CdFe_2O_4$ powder was prepared by combustion route using Citric acid as fuel. The materials used as precursors were Cadmium nitrate hexahydrate $Cd(NO_3)_2 6H_2O$, $Fe(NO_3)_2 6H_2O$ Iron nitrate hexahydrate (all these were procured from A.R. Grade of Qualligen) and Citric acid (Nuclear band). Citric acid possesses a high heat of combustion. It is an organic fuel and provides a platform for redox reactions during the course of combustion. Initially the Cadmium nitrates, Iron nitrates and Citric acid are taken in the 1:1:4 stoichiometric amounts and dissolved in 250 ml beaker slowly string with glass rod clear solution was obtained. Solution formed was evaporated on hot plate in temperature range 70^0C to 80^0C gives thick gel. The gel was kept on a hot plate for auto combustion and heated in the temperature range 170^0C to 180^0C. The nanocrystalline $CdFe_2O_4$ powder was formed within few minutes and sintered at about 800^0C for about 4 hours got brown colour shining powder of nanocrystalline $CdFe_2O_4$ as shown in following sheet.

Measurement : Cadmium ferrites powder was ground in an agate pastel-morter to ensure sufficiently fine particle size. The fine powder was calcined at 800^0C for 24 h in air and re-ground. The thixotropic paste was formulated by mixing the resulting $CdFe_2O_4$ fine powder with a solution of ethyl cellulose (temporary binder) in a mixture of organic solvents such as butyl carbitol acetate and turpineol. The ratio of inorganic and organic path was kept as 75:25 in formulating the paste. The paste was then used to prepare thick films. The thixotropic paste was screen printed on a glass substrate in desired patterns. The films prepared were fired at 500^0C for 24 h. The sensing performance of the sensors was examined using a "static gas-sensing system. There were electrical feeds through the base plate. The heating was constant on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using relay with adjustable ON/OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensors. The output of the thermocouple was connected to digital temperature indicators. A gas inlet valve was fitted at one port of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of test gas using a gas-injecting syringe. A constant voltage was applied to the sensors, and current was measured by a digital Pico-ammeter. Air was allowed to pass into the glass dome after every Gases exposure cycle as shown in Figure (1) [14].

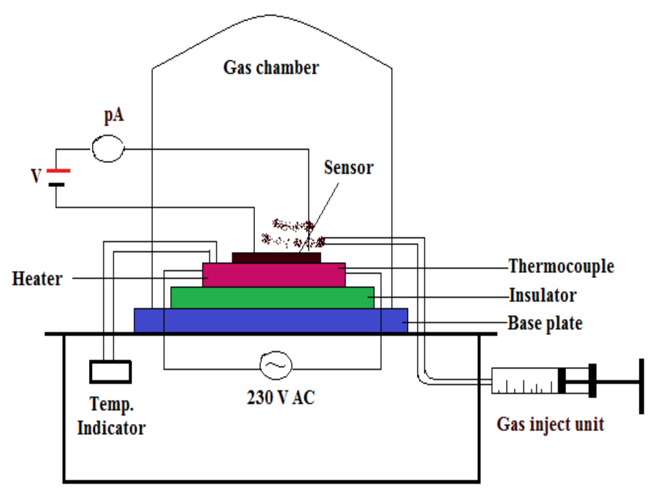

Figure (1) : Block diagram of static gas sensing setup.

Characterization Technique : The structure of the samples was checked by XRD Philips analytic X-ray B.V. (PW-3710 Based Model diffraction analysis using Cu-K_α radiation), The microstructure and morphology of the synthesized $CdFe_2O_4$ were characterized by a scanning electron microscope (SEM, JEOL JED 2300), A JEOL JEM–200 CX transmission electron microscope operating at 200 kV.

Results and Discussion : Figure (2) XRD pattern shows that the product is pure spinel type $CdFe_2O_4$ with a cubic structure. The diffraction data had shown good agreement with JCPD card of $CdFe_2O_4$ (JCPDS No.24-1016) the average crystallite size of $CdFe_2O_4$ spinel powder was estimated with the help of Scherrer's equation

$t = 0.9\lambda / \beta \cos\theta$.

The average crystallite size of nanocrystallite $CdFe_2O_4$ was ~ 64 nm [15]. Figure (3a) shows the SEM image of the as synthesized $CdFe_2O_4$ nanopowder. It is observed that $CdFe_2O_4$ have uniformed size. The surface was smooth, spongy and pores were shown in the micrograph. Feature of the nanopowder was also examined by TEM; the result in Figure (3b) shows a typical characteristic of nanopowder spheroidic particles (~ 60 nm) which agree with the TEM results.

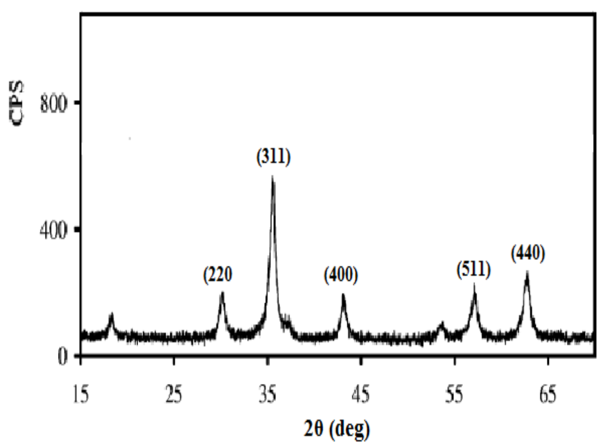

Figure (2) : X-ray diffraction patterns of $CdFe_2O_4$ as synthesized Powder

Our investigations focus on the ethanol vapour sensing properties of the $CdFe_2O_4$. The inserted of Figure (4) show a schematic image of the sensor structures. The $CdFe_2O_4$ exhibit high sensitivity and rapid response / recovery characteristics to ethanol vapor at 350°C, as shown in Figure (4). The sensitivity is about 12.23, 21.32, 36.55, and 59.23 to 50, 100, 150 and 200 ppm ethanol vapour, respectively.

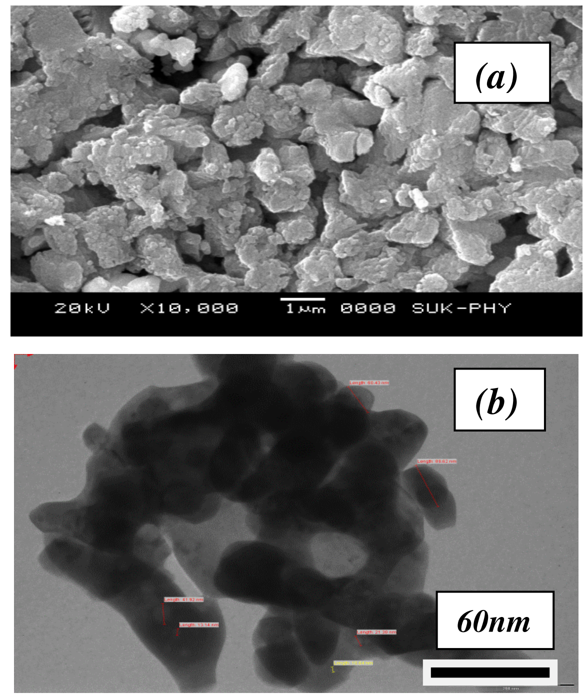

Figure (3) : (a) SEM and (b) TEM images of the $CdFe_2O_4$ nanopowder.

These results reveal that the sensor can detect ethanol vapour at different concentrations and down to 10 ppm. Furthermore, it can also be seen that the electrical signal from the sensor becomes stable within 40 s after it is exposed to ethanol vapour, and returns to the original values within 50 s after the tested ethanol vapour is replaced with air. The rapid response and recovery of the sensor is based on products can facilitate fast mass transfer of the analyte molecules, from the interaction region and also require charge carriers to traverse the barriers introduced by molecular recognition along the nanofilm. Simultaneously, comparing with nano films, the interfacial areas between the active sensing region of the nanofilm and the underlying substrate is greatly reduced. Those advantages lead to significant gain in the sensing performances of prepared nanofilm. The sensitivity of the $CdFe_2O_4$ versus ethanol vapour concentration is shown in Figure (4). The sensitivity rapidly increases with increasing ethanol vapour concentration below 200 ppm. Above 200 ppm, the sensitivity slowly increases with the ethanol vapor concentration, indicating the sensor becomes more or less saturated. Finally the sensitivity reaches saturation at about 200 ppm. Moreover, in Figure (4) shows the linear calibration curve in the range of 150–200 ppm, which further confirms that the $CdFe_2O_4$ can be used as a promising material for ethanol vapor sensors. In fact, the sensitivity of a semiconductor metal oxide is usually depicted as S=A[C] N+B, where A and B are constants and C is the concentration of the target gas or vapour. N usually has a value between 0.5 and 1.0, depending on the change of the surface species and the stoichiometry of the elementary reactions on the surface **[12]**. As shown in Figure (4), a linear relationship between sensitivity and the ethanol concentration can be observed, indicating that N=1.0 for the $CdFe_2O_4$. Most of the semiconductor metal oxide sensing materials operate on the basis of the modification of the electrical properties of active element, which is brought about by the adsorption which an analyte on the surface of the sensor. Normally, the O_2 molecules, which are chemisorbed and dissociated on the surface of semiconductor metal oxides, can generate oxygen species. These oxygen species lead to a decrease in the conductance of the sensing layer, resulting in a high resistance of the sensor. When the sensor is exposed to a reducing gas such as ethanol vapour, the reducing gas may react with the adsorbed oxygen molecule and increase the conductance of the sensing layer, there by the sensor response can easily found by comparing the resistance of the sensing layer in air and the target gas.

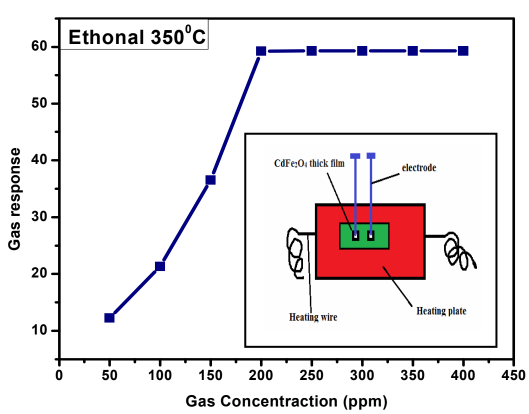

Figure (4) : Response characteristics of the $CdFe_2O_4$ film to ethanol at 350°C. The right insert shows a schematic image of sensor structure.

Discussion :

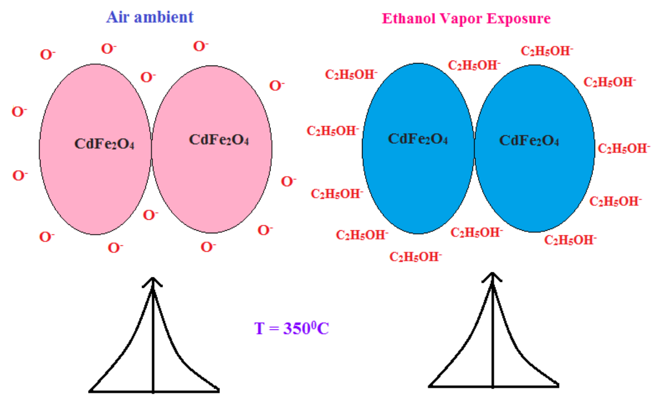

Figure (5) : Gas sensing mechanism of $CdFe_2O_4$ at 350^0C.

The working principle of the thick film semiconducting gas sensors is based on the change of the electronic conductivity of the semiconducting material upon exposure to ethanol vapors. The interaction of ethanol gas molecules with surface of thick film causes the transfer of electrons between semiconducting surface and adsorbents. The atmospheric oxygen molecule O_2 is adsorbed on the surface of the thick film. They capture the electrons from conduction band of the thick film material as

$$O_{2(air)} + 4e^- \rightarrow 2O^{2-}_{(film\ surface).}$$

It results in decreasing electronic conductivity of the film. The $CdFe_2O_4$ sample was not as per the stoichiometric proportion and all samples were observed to be oxygen-deficient. This deficiency gets reduced duo to adsorption of atmospheric molecular oxygen. This helps to decrease electronic conductivity of the film. Upon exposure, ethanol molecules get oxidized with the adsorbed oxygen ions, by following a series of intermediate stages, producing CO_2 and H_2O. This results in evolving oxygen as electrically neutral atoms trapping behind the negative charges on the film surface. Upon exposure of ethanol Vapor, the energy released in decomposition of ethanol molecule would be sufficient for trapped electron to jump increase in the conductivity of the thick film of $CdFe_2O_4$. These generated electrons and donor level in the energy band gap of $CdFe_2O_4$ will contribute to increase in conductivity. When ethanol reacts with oxygen a complex series of reactions take place, ultimately converting the ethanol to carbon dioxide and water as fallows

$$C_2H_5OH_{(gas)} + 6O^{2-}_{(film\ surface)} \rightarrow 2CO_{2(gas)} + 3H_2O_{(gas)} + 12e^-_{(cond.band).}$$

This shows n-type conduction mechanism Figure (5). Thus on oxidation, single molecule of ethanol liberates twelve electrons in conduction band and results in increase in conductivity of the sensors. Increase in operating temperature causes oxidation of large number of ethanol molecules, thus producing very large number of electron resulting conductivity increases to a large extent. This may be the reason why the gas response increases with operating temperature. The thermal energy (temperature) at which the gas response is maximum, is the actual thermal energy needed to activate the material for progress in reaction. However, the response decreases at higher operating temperature, as the oxygen adsorbates are desorbed from the surface of the sensor. Also, at higher temperature, the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for decreased gas response at higher temperature.

Conclusions : we have successfully prepared cadmium ferrite nanocrystalite by an improved combustion method. $CdFe_2O_4$ with an average diameter of 64 nm are synthesized by an combustion method. The structure of cadmium ferrite was spinel confirmed by XRD and their ethanol vapour sensing properties are also investigated by exposing the corresponding sensor to different concentrations of ethanol vapour at 350°C. High sensitivity and rapid response/recovery was observed in investigation, suggesting that $CdFe_2O_4$ are act as good candidates for fabricating high performance gas sensors.

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