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Sol-gel synthesis of TiO_2 nano powder and study of their gas sensing performance using thick film resistors

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ABSTRACT

Nano size TiO_2 powder with anatase and rutile structure was prepaired by a sol-gel method using TiCl4 ethanol solution. The $TiCl_4$ acts as precursor in this reaction. The obtained product was with grain size of 2.80 nm. The obtained product consist of both rutile and anatase phases. These phase formed after drying of gel at 80^0C. The proportion of anatase to rutile was 6:8. The high proportion of rutile phase responsible for higher gas sensitivity. The thermal stability of nano product tested using TGA-DTA technique. The nano size structure of TiO_2 was confirmed by X-Ray Diffraction Spectroscopy (XRD), Field Emission Scanning Electron Microscopy (FESEM). The gas sensitivity of material tested by preparing thick film by screen printing technique for this the thixotropic paste of material was prepared by using ethyl cellulose and butyl cellulose. The gas sensing performance of this thick film was tested for gases like ethanol, CO_2, H_2S, NH_3, CO, Cl_2, gases and observed maximum sensitivity for H_2S gas at 350^0C.

KEYWORDS

Nano TiO_2;

H_2S gas sensor

INTRODUCTION

Gas sensor devices are in demand for measuring amount of pollutant gases. For measuring pollutant gases the metal based semiconductiong oxide have been extensively used in recent year[2]. The main advantages of semiconductor metal oxide based sensor are their low price, high sensitivity, small size, low power consumption and simple measuring electronic[3]. Recently gas sensor based on semiconductiong metal oxide such as ZnO, SnO_2, TiO_2 have been found to be very useful for detecting H_2S, NH_3 and ethanol[1, 2, 3]. The gas sensitivity depends on operating temperature[2] type of material[3] size of metal oxide[2]. Sensor sensitivity can be significantly increased by using material with very small grain size[3]. The TiO_2 is the n-type semiconductiong metal oxide containing electron are majority charge carrier[9]. When oxygen adsorb on metal oxide surface it extract electron form surface thereby decreasing conductivity. When reducing gas interact with surface which gives electron back to surface that increases conductivity[2]. Thus the rate of adsorption and desorption of oxygen during gas sensing determine the sensitivity of sensor material[4]. When material having smaller size have high rate of adsorption and desorption of oxygen. The Lu et al have indicated that the SnO_2 sensor response to 500 ppm CO increases with decreasing particle size[14]. The sensitivity increases with decreasing size of oxide material due to change in surface as well as catalytic property of material. Thick and thin film is the two techniques for fabrication of semiconductiong metal based gas sensor. Thick film gas sensor has greater advantages with thin film such as low cost, simple construction and greater sensitivity[5]. In the present work we have synthesized nano TiO_2 and bulk TiO_2 and its gas sensitivity measured for NH_3, H2S, H2, Cl_2, SO_2, CO, CO_2, and Ethanol. The TiO_2 has three phases Rutile, Anatase, Brookite. The rutile phase is thermodynamically stable[9] but Brookite and Anatase are unstable at higher temperature which transfer to Rutile at higher temperature. The TiO_2 has many application in day to day life due to its unique property such as wide range of band gap3.2 ev,strong oxidative ability and non toxicity[10] such as Photo catalysis material, solar cell material[1] pigment industries[1] UV blocker[6] medicine[7] Semiconductiong material in gas sensor[2]. In this application the nano TiO_2 has greater effect than bulk TiO_2[13] thus in recent year greater intension on synthesis of nanoTiO_2. Thier are various method was developed for synthesis of nano TiO_2 1) Hydrothermal Method[10] 2)Solvothermal method[11], 3)Ultrasonic Method[7], 4)Spray paralysis[14], 5)Sol-Gel Method[10] 6) Chemical vapor deposition[10]. 7)Co precipitation[7], 8)Flame hydrolysis[7] Out of which the sol-Gel method has greater advantages. In sol gel method the metal alcoxide hydrolyses by organic or inorganic reagent in present of organic or inorganic solvent[7, 11, 12]. In sol-Gel reaction hydrolysis and condensation reaction take place when metal alcoxide react with hydrolyzing reagent[9]. The rate of hydrolysis and condensation determine the size of product. These two processes depends on experimental condition such as PH[9], concentration of reagent[1], temperature[10], stirring rate[9] etc. Thus by controlling this condition the size of product can control in sol-gel method thus this method has greater advantages than other method[1]. In present works our research group target to synthesize nano TiO_2 by two different sol gel route. We also represent the gas sensing property of this two product because the size of product has greater effect on gas sensing property. X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), ultraviolet diffuse reflectance spectroscopy (UV-DRS) Thermogrvimetry analysis-Differential Thermal analysis (TGA-DTA) technique where used for characterization of material.

EXPERIMENTAL

Synthesis

All the chemical were analytical grade.1.5 ml $TiCl_4$ was slowly added drop wise into 15 ml ethanol at room temperature. A large amount of HCl gas was exhausted during the mixing process. A light yellow solution was obtained and gelatinized for several days to form sol-gel. The sol-gel solution was vaporized at 80^0C until a dry gel was obtained. The dry gel precursor was calcined at different temperature for definite time in air to form TiO_2 powder.

Preparation of thick film

The gas sensitivity of prepaired material was tested by using thick film. The thick film of material was prepaired on glass substrate using thixotropic paste of material. The thixotropic paste of material prepaired by taking 0.1mg compound, 1 gm ethyl cellulose(Binder) and 1 ml of organic solvent (4:3:3 Butylcellulose: Butylcarbitolacetate: Terpenol). The film with uniform thickness was prepaired by applying constant pressure on screen printing. The films were fired at 350^0c for one hr. to remove organic part.

Characterization

The crystal structure of material were studied using X-ray diffraction technique (XRD make BRUKER). For analysis Cu- K radiation used with wavelength $1.5406A^0$ with angular region $20\text{-}80^0$. The band gap of compound were calculated using UV-diffuse reflectance spectroscopy(UV-DRS make) The prepaired material were confirmed by studying FTIR spectra of prepaired material. The FTIR spectra were taken on FTIR model SHIMADZU no.2328). The surface morphology and chemical composition of compound were studied on scanning electron microscope (model SEM, JEOL, JED 6300) coupled with energy dispersive spectrometer (model EDS, JEOL, JED 2300). The thermal stability of two compound were tested using thermo gravimetric and differential thermal analysis technique in presence of nitrogen gas (model Mettler Toledo Star 801). The temperature range for thermal analysis are 25-800^{0}c at heating rate 10^{0}c min^{-1}. The –Al_2O_3 used as reference for this analysis.

RESULT AND DISCUSSION

X-Ray diffraction analysis

The Figure 1 shows the XRD pattern of sample. The XRD pattern were matched with JCPDS card No.21-1272 XRD pattern. The XRD pattern for compound revels that compound has tetragonal pahase. The peak broadening are due to nano size.

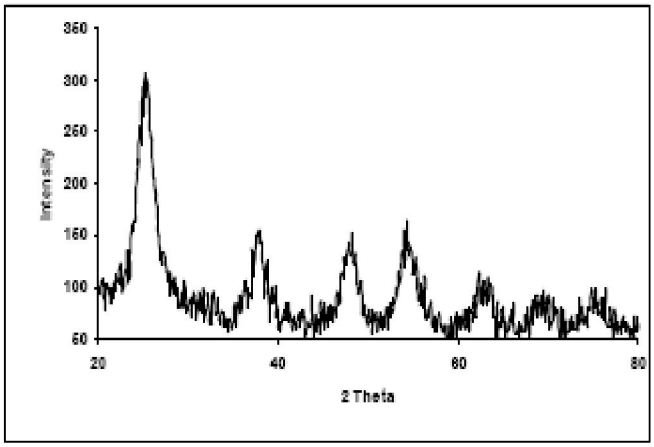

Figure 1 : XRD pattern of nano size TiO_2

The crystal size was calculated by applying sherrer equation (Patterson, 1939)[8]as follows

$$L = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

Where L is crystallite size (nm)

K is constant whose value is approximately 0.9

λ is wavelength of X-ray radiation source (0.1542 nm for Cu Ka)

β is line width at half- maximum height (radian)

θ is the Bragg's angel at the position of the maximum peak

The percentage composition of Anatase (%X_A) and Rutile (%X_R) phases calculated by Liqiang's equation[8] as follows

$$\%X = \frac{10_{o}}{1+1.265\frac{I_R}{I_A}} \quad (2)$$

And $\%X_R = 100 - \%X_A$

Where %X_A is the percentage of Anatase phase in TiO_2

%X_R is the percentage of Rutile phase in TiO_2

I_A is the intensity of Anatase peak at 2θ =

I_R is the intensity of Rutile peak at 2θ =

The Unit Cell Parameter(a,c,Unit Cell Volume) was calculated[8] as follows

$$\frac{l}{d^2} = \frac{h^2+k^2+l^2}{a^2c^2} \quad (3)$$

And Unit cell Volume

$$V = a^2c \quad (4)$$

Where d is the distance between two lattice planes (nm) which calculated from Bragg's law as follows

$$n\lambda = 2d\sin\theta \quad (5)$$

h,k,l are the miller indices which is characteristics value from each 2θ

V is the unit cell volume (nm^2)

a,c is Unit cell side(nm)

n is the integer called order of reflection (n=1)

λ is wavelength of X-ray radiation source (0.1542 nm for Cu Ka)

θ is the Bragg's angel at the position of the maximum peak

Field emission scanning electron microscopy analysis

The sample for this analysis was prepared by coating the sample of any thickness on alumina stub. The electron beam scan over the surface of sample to obtain the image of surface due to this size measured by FESEM was greater than size measured by TEM. The result of this analysis is represented in Figure. The SEM

TABLE 1

	Crystal size(nm)	% of X_A	% of X_R	d_{101}(nm)	a(nm)	c(nm)	Volume (nm^3)
1	2.80	60.64	80.58	0.1812	0.1902	0.4928	0.0178

alculated value form XRD data

image shows spherical nature of product and particle dimension about 2.96nm. The result of EDSEnergy Dispersive Spectroscopy) anaysis shown in TABLE. From graph of EDS analysis it is cleared that the total percentage of oxygen specis was 21.58% and Titanium specis was 78.42%

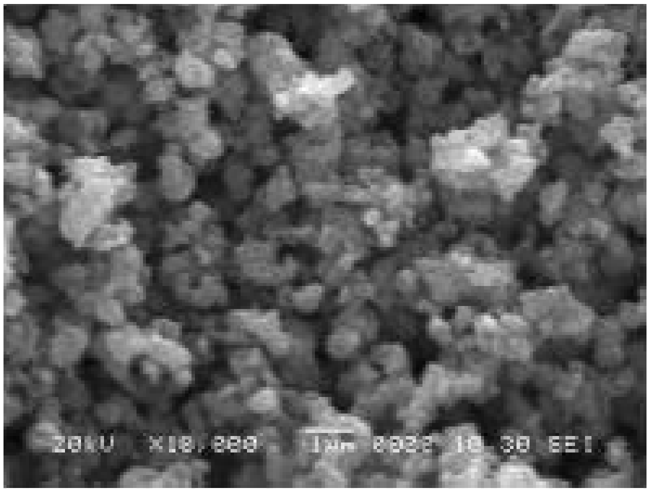

Figure 2 : FESEM Images of nano size TiO_2

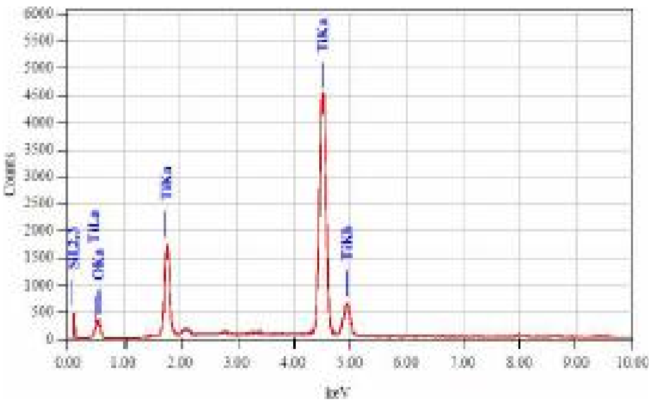

Figure 3 : EDS of Nano TiO_2

Thermogravimetric and differential scanning thermal analysis

The precipitate from sol0gel processing of titania were amorphous in nature. A significant weight loss was observed in TGA curve for dried titania gel at 741^0c undergoing total weight loss of 7.56% between two analyzed temperature $100-800^c$c. Upto 441^cc no significant weight loss observed in in titania that is up to 441^c the sample thermally stable. After 441^0c the weight loss started and simple get decomposed between temperature 442 -741^0c. The weight loss between 100-44^0c was due to removal of loosely bounded water molecule in gel network. The decomposition step between 441-741^0c due to decomposition of chloride species and dehydration of the gel. A DTA pattern was complementary to the TGA observation. The very small exothermic peak centered around 5510c represent the decomposition of chloride species. Along with dehydration of titania gel. This was supported by corresponding weight loss in TGA curve

TABLE 2

Element	Weight%	Atomic%
O K	21.58	45.17
Ti K	78.42	54.83
Total	100	

Weight of Oxygen and Titanium in sample

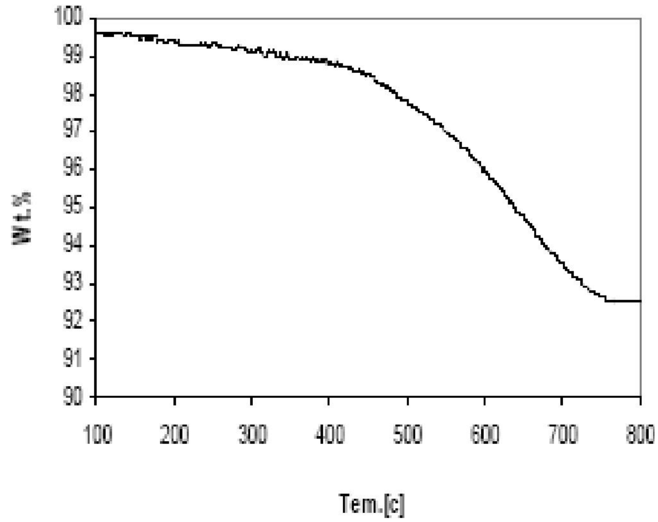

Figure 4 : TGA of Nano TiO_2

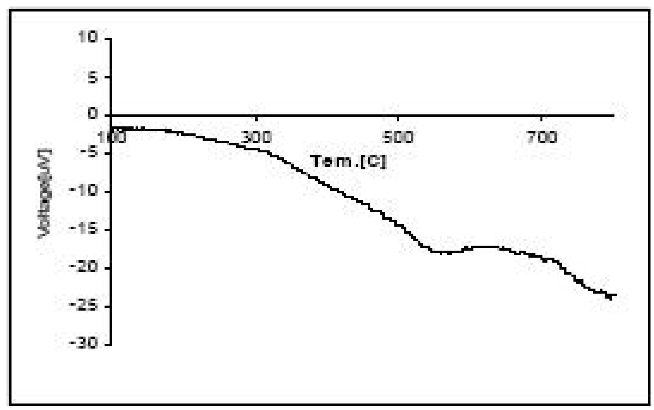

Figure 5 : DTA of Nano TiO_2

IR spectroscopic study

The Figure represents the FT-IR spectra of sol-gel synthesized product. The peaks at 3400 and 1650 cm^{-1} in the spectra are due to the stretching and bending vibration of the –OH group. In the pure TiO_2 spectrum peak at 550cm^{-1} shows stretching vibration of Ti-O and peak at 1450cm^{-1} shows stretching vibration of Ti-O-Ti .

UV-DRS spectroscopic study

The UV-DRS technique was used to determine the absorption peak value for nano TiO_2. From the Figure 6. It is observed that absorption value was 330 nm.

The UV absorption value for bulk TiO_2 was taken form reference and ti was around 410nm. From this it is cleared that there is blue shift(shifting of wavelength to lower value). The band gap of compound was calculated by using following equation

$$E = \frac{hc}{\lambda}$$

The Band gap value for nana TiO_2 was 3.76nm

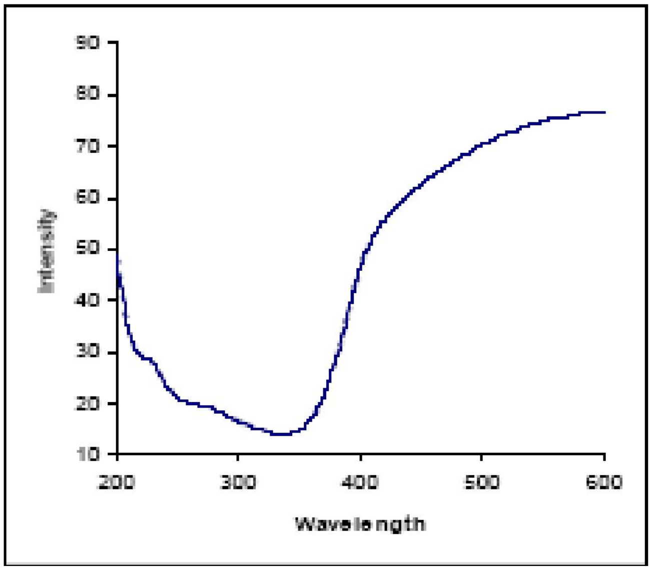

Figure 6 : UV-DRS spectra of Nano TiO_2

Gas sensing performance of Nano TiO_2

Detailed of gas sensing system

The gas sensing performance of the thick film was measured by using static gas sensing unit This apparatus consists of heater plate fixed on the base plate to heat the sample under set up to required temperature. The Cr-Al thermocouple was used to sense the gas at operating temperature of the sensor. The output of thermocouple was connected to a digital temperature recorder. A gas inlet valve was fitted at one of the port of the base plate. The required gas concentration inside the static system was achieved by injecting the known volume of a test gas using gas injecting syringe. A constant voltage was applied to the sensor and current was measured by a digital Pico ammeter. Air was allowed to pass into every gas exposure cycle.

Gas sensitivity of Nano TiO_2

The sensing mechanism of based on change in conductance by exposing the gas on semi conducting material. The TiO_2 is an n-type semiconductor. It consists

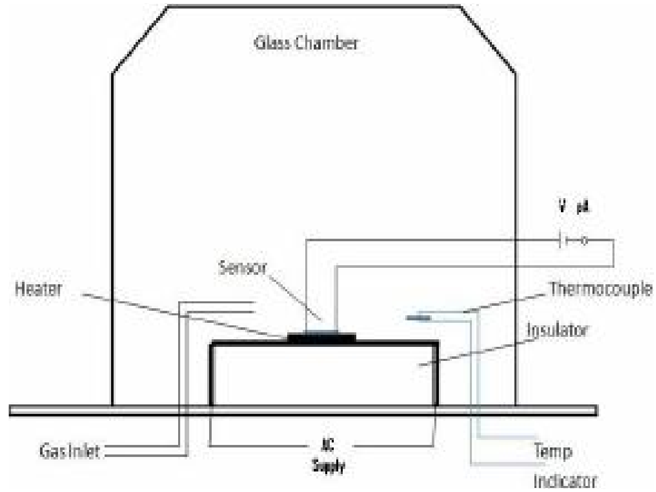

Figure 7 : Static gas sensing unit

of electron as majority charge carrier. When O_2 adsorbed at the surface it extract electron from surface. Thus reduces the electron in conduction band leading to decrease in conductivity of material. When O_2 adsorbed on surface it convert to O^- and O^{2-}. The H_2S gas is reducing gas which reduces species O^- and O^{2-} to O_2 during this process electron again given back to semi conducting surface. Thus conductance of system increases when H_2S gas exposed. The following reaction taking place during adsorption and desorption process

Adsorption

$$O_2 + e^- \longrightarrow 2O^-$$

$$O_2 + e^- \longrightarrow 2O^{2-}$$

Desorption

$$H_2S + 2O^- + O^{2-} \longrightarrow H_2O + SO_2 + e^-$$

Thus NH_3 possess high reducing property than other gases. The gas sensitivity of different gases is determined between 100- 500 °C by passing the known amount of gas in gas sensing system . At 350 °C adsorption desorption rate was high than other temperature as compared to other temperature hence all gases shows good sensitivity at that temperature. gases the H_2S gas shows high sensitivity. The gases like H_2S, NH_3, Cl_2, CO, CO_2, and gaseous ethanol were tested and the comparative study is shown in Figure. The change in resistance before passing the gas and after passing the gas was measured for all gases. From this data the sensitivity was calculated by formula as:

$$S = \frac{(Ra - Rg)}{Ra} = \frac{\Delta Ra}{Ra} \quad (6)$$

Where, Ra and Rg are the resistance of a sensor in air and the test gas, respectively

The sensitivity was determined for all gases and the graph of sensitivity versus temperature is plotted, which indicates that, the highest sensitivity is for H_2S gas at 350 °C (Figure 7)

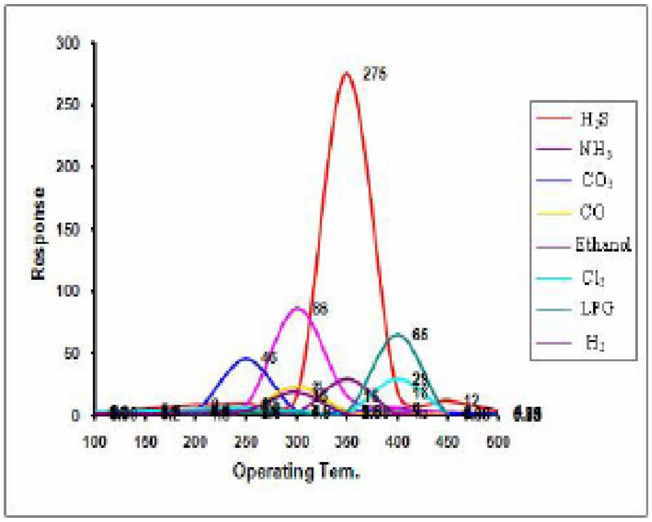

Figure 8 : Sensitivity of Nano TiO_2

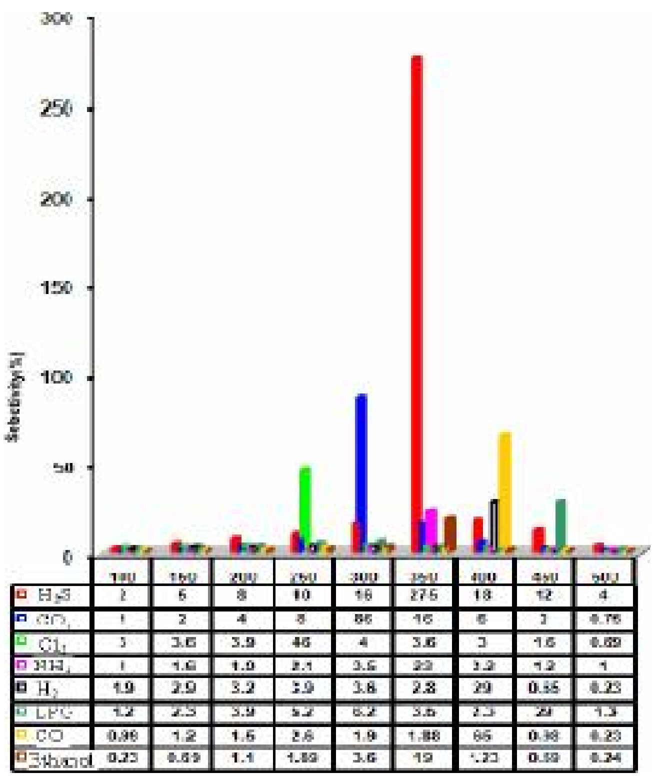

Figure 9 : Selectivity of Nano TiO_2

Selectivity of Nano TiO_2

The ability of sensor to respond to a certain gas in the presence of other gases is known as selectivity. The Figure show gas selectivity for nano TiO_2. It is cleared form graph the highest selectivity for H_2S gas at 350°c

CONCLUSIONS

Sol-Gel method in which $TiCl_4$ethanol solution use as precursor are best method for synthesis of mixed rutile and anatase phase nano TiO_2. The size of product controlled by controlling the concentration of $TiCl_4$. The H_2S gas response increase with increasing temperature up to 350°c and after that response decreases.

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