VOLUME - VIII, ISSUE - I - JANUARY - MARCH - 2019
AJANTA - ISSN 2277 - 5730 - IMPACT FACTOR - 5.5 (www.sjifactor.com)

5. Synthesis and Characterization of TiO_2 Nanoparticles

C. R. Yewale
Department of Physics, S.P.H. Arts, Science & Commerce College, Nampur Dist. Nashik, Maharashtra.
A. V. Gajbhiye
Department of Physics, S.P.H. Arts, Science & Commerce College, Nampur Dist. Nashik, Maharashtra.
D. F. Shirude
Department of Physics, S.P.H. Arts, Science & Commerce College, Nampur Dist. Nashik, Maharashtra.
R. P. Shewale
Department of Physics, S.P.H. Arts, Science & Commerce College, Nampur Dist. Nashik, Maharashtra.

Abstract

In this paper, TiO_2 nano powder prepared by hydrothermal synthesis process. XRD confirms the fine crystalline formation. The sensors are prepared in the form of thick films prepared by screen-printing technique on chemically clean optically plane glass substrate. All the devices were tested and finally concluded that the (TiO_2- HCOOH) exhibited high sensitivity and fast response time to CO at 250°C. In all the samples, the sensitivity increases by increasing concentration of CO gas in ppm. The resistance of thick films decreases by increasing concentration of CO gas in ppm at room temperature due to surface oxygen vacancies of TiO_2 act as electron donors. The sensitivity, selectivity, response time and recovery time of the sensor were measured and presented.

Keywords: Nano-Particles, TiO_2, Hydrothermal, Sensitivity.

1. Introduction

Nanostructure semiconductor metal oxides, such as SnO_2, ZnO, TiO_2, and NiO, are promising sensing materials for a wide range of gases and vapors. The enhanced sensing features are determined by the high chemical activity and porosity of the active materials, which are direct consequences of their nanostructure. Because of this, gas sensing capabilities depend critically on the synthesis method and parameters that allow for tailoring of selectivity and sensitivity toward the target species. These materials can be further developed into

Nanocomposites, which are materials where metal nanoparticles(NPs) are dispersed in a matrix of metal oxides. The NPs play both passive and active roles in the sensing process. The presence of NPs increases the active surface area and improves gas diffusion inside the film. Nanocomposites have physical properties that differ from those of the nanostructure single phase oxides and improve the conditions for sensing by reducing the electrical resistance and increasing the optical absorption. Nano-crystalline materials with particle size smaller than 100 nm exhibit amazing properties which are not found in conventional materials. One of the distinctive features, the main one for gas sensors, is an extremely large specific surface area. Oxide semiconductor films are promising for gas sensors due to the dependence of their electrical conductivity on the environmental gases such as O_2, CO, H_2……. Titanium dioxide is being used in a great variety of applications. It has been investigated for humidity and gas-sensing behavior. It has three different crystallographic forms: brookite, anatase and rutile. Anatase is metastable and converted irreversibly into rutile at high temperature. Its preparation is fundamental to obtain properties suitable for gas-sensing applications such as: structural stability, porosity and high surface-to-volume ratio in order to emphasize surface effects. The sensing properties of TiO_2 films are based on surface interactions of reducing or oxidizing species, which affect the conductivity of the films. Films of Nano-sized TiO_2 could be achieved by different techniques such as sputtering in reactive atmosphere followed by thermal annealing at 800°C, Sol-Gel, Spray Pyrolysis, Screen Printing, Laser Ablation, etc. The main purpose of this paper is to prepare low cost Nano-sized TiO_2 films with structural and electrical characteristics suitable for sensing oxidizing and reducing gases.

Application of TiO_2

1. TiO_2 is an effective pacifier in powder form, where it is used as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines, as well as toothpastes.
2. In cosmetics and Skin care products, it is used both as a pigment, sunscreen and a thickener because of its high refractive index, its strong UV light absorbing capabilities and its resistance to discoloration under UV.
3. It is particularly in Anatase form, it is a photo catalyst under UV light. It is most efficient and environmentally benign photo catalyst. It is semiconductor which turns to a high energy state by receiving light energy, and releases electrons from its illuminated surface.
4. It is used for anti-fogging glasses, self cleaning glass, anti bacterial, anti-

viral, fungicidal, antisoiling, self cleaning, air purification, water treatment, water purification. It is used in electronic components like capacitor.

Experimental Work

Hydrothermal Synthesis of TiO_2

There are several ways of preparing TiO_2 particles. The hydrothermal method has many advantages like producing a highly homogeneous crystalline product, which can be obtained directly at relatively lower reaction temperature (<150°C). Its most important feature is that it favors a decrease in agglomeration between particles, narrow particle size distributions, phase homogeneity, and controlled particle morphology. . It also offers the uniform composition, purity of the product, monodispersed particles, and control over the shape and size of the particles, and so on. The hydrothermal technique has been found to be one of the best techniques to prepare TiO_2 particles of desired size and shape with homogeneity in composition and a high degree of crystallinity. Hence, the authors have carried out the synthesis of TiO_2 under hydrothermal conditions and have used the material in the degradation of organic compounds.

The synthesis of TiO_2 is usually carried out in small autoclaves of Morey type, provided with Teflon liners. The conditions selected for the synthesis of TiO_2 particles are: $T = < 200°C$, $P < 100$ bars. Such pressure, temperature conditions facilitate the use of autoclaves of simple design provided with Teflon liners. The use of Teflon liners has helped to obtain pure and homogeneous TiO_2 particles. Though the experimental temperature was low ~ 150°C, TiO_2 particles with a high degree of crystallinity and the desired size and shape could be achieved through a systematic understanding of the hydrothermal chemistry of the media. Here it is appropriate to mention that the size of the Titanium particles is a most critical factor for the performance of the material in the photo catalytic activity, and the monodispersed nanoparticles are the most suitable ones. It has been shown that the particle size is a crucial factor in the dynamics of the electron/hole recombination process, which offsets the benefits from the ultrahigh surface area of nanocrystalline TiO_2. The dominant e-/h+ recombination pathway may be different for TiO_2. Different particle size regimes have been established for improving the photo catalytic efficiency s of different systems.

The starting materials such as that of TiO_2 and the solvent with definite molarities (1.5 to 4.0 m) were taken in a Teflon liner. The internal pressure was maintained below 100 bars through percent fill in the liners. The starting mixture was stirred thoroughly to obtain a homogeneous and relatively viscous solution, which was later kept inside an autoclave and heated at 150°C for about 40–48 hours. Several solvents like NaOH, KOH, HCl, HNO_3, HCOOH and H_2SO_4 were treated as mineralizers and it was found that HNO_3 is a better mineralizer for obtaining monodispersed nanoparticles of titanium with homogeneous composition under the present experimental conditions. The authors have used different starting charges such as reagent grade anatase, sintered anatase (at about 800 to 900°C for 10 hours), and $TiCl_4$ and titanium gel. In each case, the resultant product was TiO_2, however, with different ratios of rutile and anatase depending upon the charge, as confirmed from the x-ray powder diffraction studies. Though the rutile phase was more dominant in the resultant product, the presence of a small amount of anatase persisted except when the experimental temperature was approximately 200°C. When sintered anatase or titanium gel was used as charge, it yielded better results, for example, the resultant product contained more or less uniformly sized or monodispersed particles with a high degree of crystallinity, and interestingly, the rutile phase was formed as a prominent phase with a better yield. Better results, in this sense, meant good photo catalytic activity because of the monodispersed particles with a high degree of crystallinity. Similarly, the authors have tried $TiCl_4$ as charge, and the resultant product contained both anatase and rutile. The formation of a single phase required the proper selection of Ph of the media and crystallization temperature. The present authors have carried out the TiO_2 synthesis within a wide range of pH values of the media. When the pH of the medium was low (pH = 1 to 2) only rutile phase was formed. When the pH was kept even lower, i.e., in the negative range, the product contained a small amount of anatase also. As the pH of the medium was increased, the product contained essentially anatase with very little rutile. Thus, with the addition of KOH or NaOH, the formation of anatase phase was favored. With a further increase in the pH, i.e., beyond twelve, in the present experimental temperature, only amorphous material was obtained. Raising the temperature results in the formation of alkali titanates. Table 1 gives the results of the mild hydrothermal experimental preparation of ultrafine particles of TiO_2. Thus, it is necessary to maintain a proper acidity in the system in order to obtain a homogeneous rutile phase. Similarly, control over the temperature, time, and pH of the medium helps in the preparation of a desired particle size and shape. When the reaction temperature and time were increased, it resulted in the formation of faceted grains of bigger size. Fig.3 shows the representative photographs of TiO_2 particles prepared under hydrothermal conditions.

Results and Discussion

The materials used for gas sensors are generally prepared in the form of bulk, pellet or a film (thin or thick). The films were deposited on glass substrates. In this present study, the sensors are prepared in the form of thick films prepared by screen- printing technique on chemically clean optically plane glass substrate It is most simple and less expensive way of preparing the sensors as compared to chemical vapor deposition, thermal evaporation, etc. methods. After hydrothermal synthesis fine powder was formed. The paste was prepared by mixing synthesized fine powder with ethyl cellulose and binder for screen-printing. The paste was screen-printed on the glass substrate in the form of thick film having thickness of the order of 16 – 24 microm. The films were subjected to heating at 100°C for an hour to decompose intermediate compounds. For surface resistance measurement, electrodes of conducting silver paint were formed on adjacent sides of the film and then the films were subjected to heating at 500°C for 1 hrs for firing.

Thermal Runway

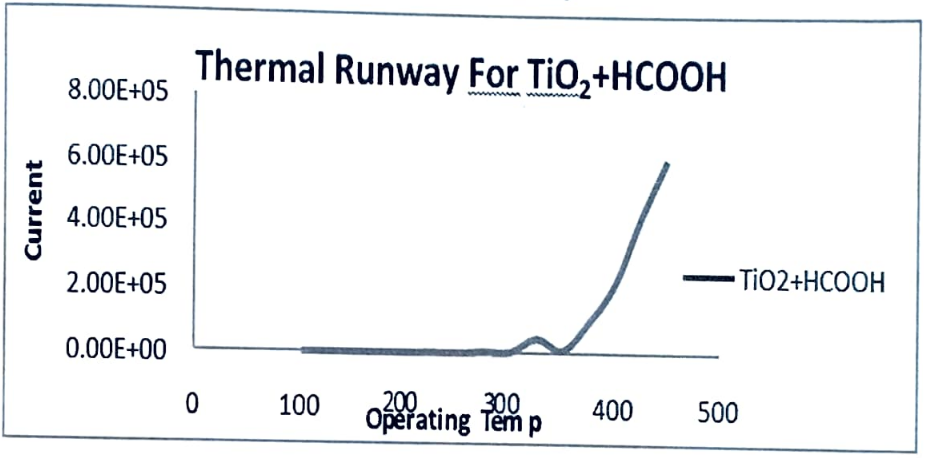

Figure 1

X-ray Diffraction (XRD

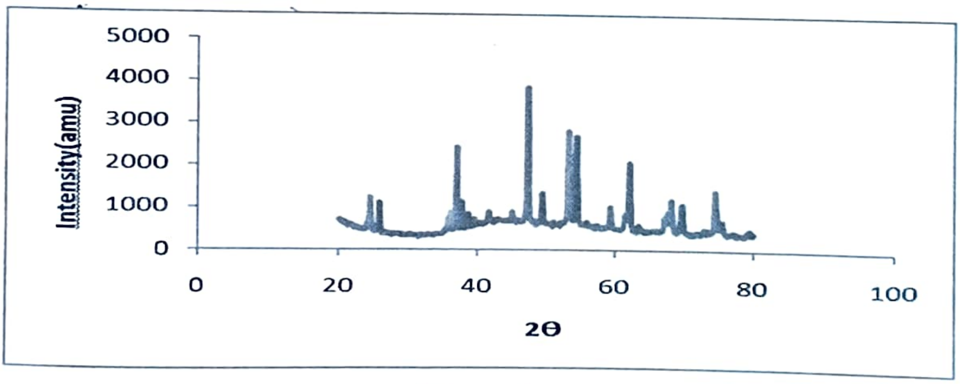

Figure 2

The XRD studies were carried out by using a RIGAKU model DMAX-2500 X-ray diffractometer.The X-ray powder diffraxtion technique is preferred and used for bulk material to understand the different phases, structure and also to calculate crystal size. The XRD gives „d" values which are used for identification of different phases and corresponding structure of the material present in the sintered or pellet.XRD also used to calculate the particle size.

The peaks in XRD-graph show the formation of fine crystalline nanoparticles. Grain Size:-

$$\text{Peak} = \frac{pmk}{2} = \frac{3861}{2} = 1930$$

$$2\square = 47.$$

$$\square = \frac{47.2468}{2} = 23.6234$$

$$B_{1/2} = \text{Max. Intensity} - \text{Min. Intensity}$$

$$= 47.4457 - 47.1474$$

$$= 0.2983$$

$B_{1/2}$ in radians:

$$\frac{180}{\square} = \frac{rad}{x}$$

$$X = \frac{\theta}{180} \times \pi \text{ rad}$$

$$X = 0.4121 \text{ rad}$$

$$X = \frac{23.6234}{180} \times 3.14$$

Therefore, Grain Size $= \dfrac{0.9 \times 1.54}{0.4121 \times \cos(23.6234)} = 3.671$ nm

SEM (Scanning Electron Microscopy)

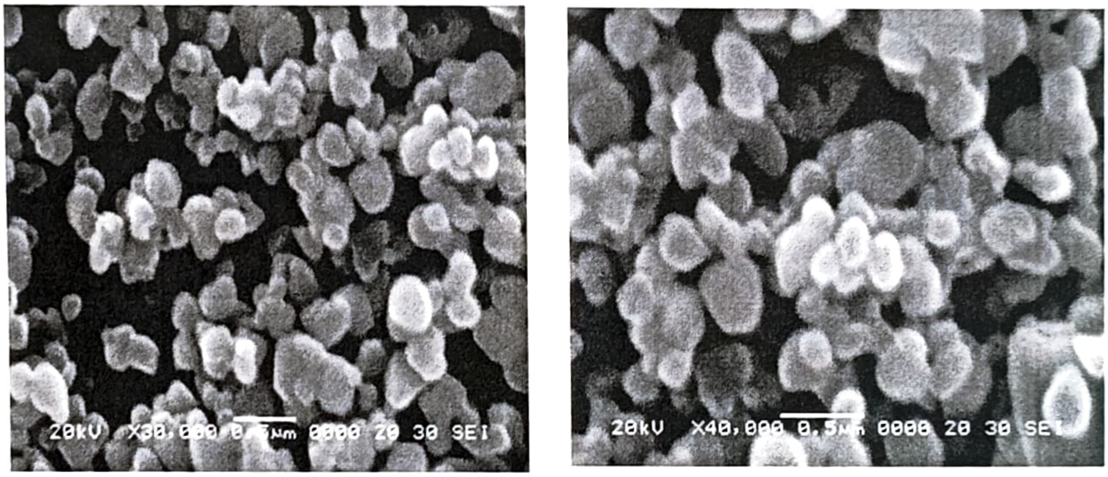

Figure 3. SEM Images of unmodified TiO_2 Thick Film

Above two figures shows that the SEM images of TiO_2 thick film fired at 500°C. The film consists of voids and a wide range of particles with particle sizes ranging from 200 to 1330 nm which are uniformly distributed over the substrate surface. We can also see some flower like structures in them.

Electrical Conductivity

The dependence of conductivity of TiO_2 thick films with temperature in air and CO ambient. Electrical conductivity of these films goes on increasing with increase in temperature in air and gas (CO) ambient, indicating Negative temperature This shows the semiconducting nature of the films.

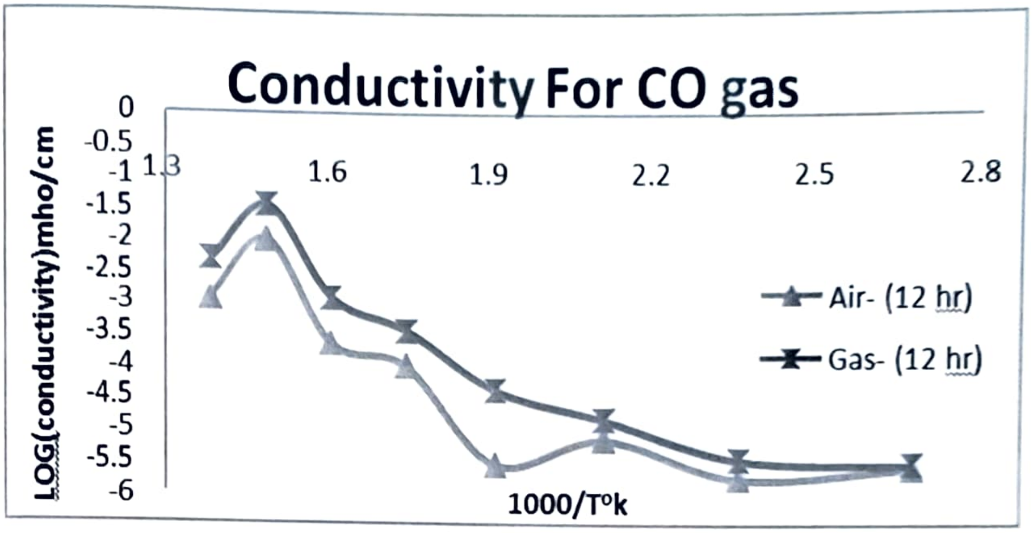

Figure 4

Selectivity

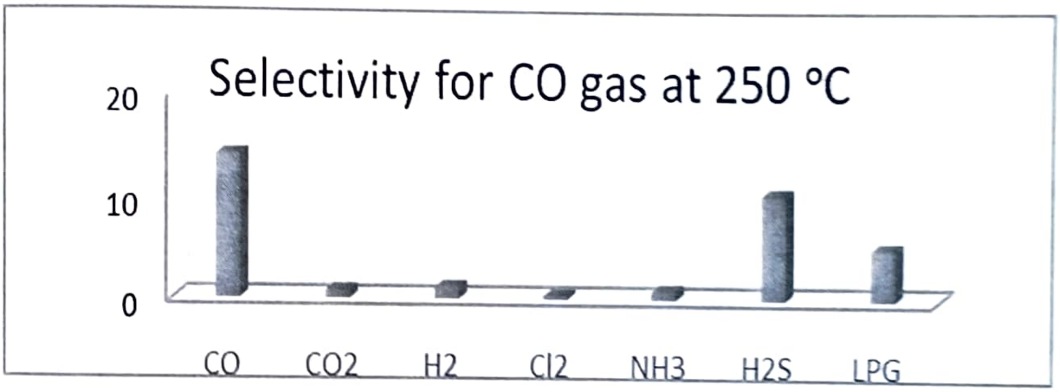

Figure 5

The ability of the sensor to respond to a specific gas in the presence of other gases is the selectivity.

Sensitivity

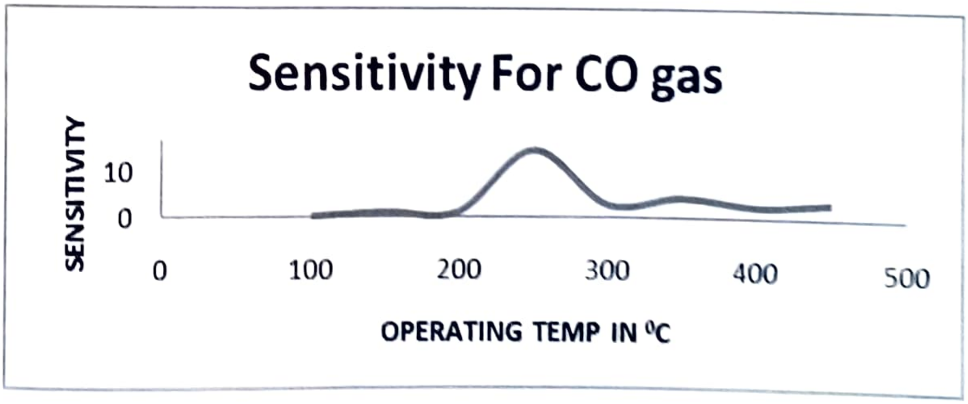

Figure 6

Correlation between CO sensitivities and Surface reactivities, both the changes in the relative resistance of anatase film upon exposure to CO gas and the recovery of resistance upon turning the CO off can be related to the chemical changes occurring on the Titania surfaces.

Sensitivity with Operating Temperature

Figure 6 shows the variation in the sensitivity to CO gas (300 ppm) with operating temperatures (for films of various thicknesses). It is noted from the graph that response increases with increasing temperature, and attains a maximum at 250°C, and decreases with further increase in operating temperature for all thicknesses and a film thickness of 33 m is found to be most sensitive for sensing CO gas.

Conclusions

The considered applications and particular features of metal-oxide gas sensors allow us to formulate some general trends in this actively developing field of science.

There is a clear tendency to search for new types of metal oxide nanostructures, including nanowires, nanobelts, and nanorods that promote the use of new synthetic techniques for preparation of novel sensor materials.

There has been an increase in the number of different dopants, particularly various metal and metal oxide nanoparticles and substrate materials. These approaches are aimed at increasing the sensitivity and selectivity of metal-oxide gas sensors.

Much effort is being made to extend the working temperature range of metal-oxide gas sensors and lower the optimal working temperature to 20-25°C. The goal of these investigations is to decrease the power consumption of sensor elements.

Finally we may conclude that the thick film (TiO_2 +HCOOH) has high sensitivity and fast response time to CO at 250 °C temperature. In all the films the sensitivity increases linearly for the lower concentration range but for higher concentration range it deviates from linearity. The resistance of thick films decreases by increasing concentration of COgas in ppm at 250°C temperatures due to surface oxygen vacancies TiO_2 act as electron donors.

References

1. G. H. Jain, L. A. Patil, P. P. Patil, U. P. Mulik and K. R. Patil, *Bull. Mater. Sci.*, vol. 30, 9-17, 2007.
2. V. E. Bọchenkov, G. B. SergeeV, "sensitivity, selectivity, and stability of gas- sensitive metal-oxide nanostructures", vol.3, 31-52, 2010.
3. M. Malekshahi Byranvanda, A. Nemati Kharata, L. Fatholahib, Z. Malekshahi Beiranvand, *Journal of Nanostructures*, 3, 1-9, 2013.

4. A. K. Yewale, F.C. Raghuwanshi, N.G. Belsare, R. V. Waghmare, R. V Joat, T. S.Wasnik, K.B. Raulkar, A. S. Wadatkar, , G. T *Lamdhade, *International J. Adv. Eng. Tech.*, 2, 4, 226-230, 2011.
5. N. Barsan, U. Weimar, "Understanding The Fundamental Principles Of Metal Oxide Based Gas Sensors; The Example Of Co Sensing With Sno_2 Sensors In The Presence Of Humidity", *J. Phys. Cond. Matt.*, 15, R813, 2003.
6. Radecka Marta, Zokrzewska Katavzyna, Rekas Mieczyslaw, "SnO_2-TiO_2 Solid Solutions For Gas Sensors, Sensors And Actuators B", 47, 194-204, 1998.
7. Hokyong Shon, Sherub Phuntsho, Yousef Okour, Dong-Lyun Cho, Kyoung Seok Kim, Hui-Jie Li, Sukhyun Na, Jong Beom Kim, And Jong-Ho Kim, *J. Korean Ind. Eng. Chem.*, 19, 1, 1-16, 2008.
8. Handbook Of Hydrothermal Technology: A Technology For Crystal Growth And Materials Processing By K. Byrappa, University Of Mysore, Manasagangotri Mysore, India And Masahiro Yoshimura, Tokyo Institute Of Technology, Yokohama, Japan., 2001.