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Cl_2 GAS SENSING PROPERTIES OF Ag-SENSITIZED TiO_2 FILMS PREPARED FROM BIO-INSPIRED NANOCRYSTALLINE TiO_2

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ABSTRACT

This communication presents Cl_2 gas sensing characteristics of Ag-modified TiO_2 films, wherein TiO_2 nanoparticles (NPs) were synthesized by using bio-inspired green method. The TiO_2 NPs were characterized by using X-ray diffraction, field emission scanning electron microscopy and UV-visible spectroscopy respectively for their structures, morphologies, and optical properties.The TiO_2 films were prepared by using Doctor's Blade method and sensitized by using Ag. The average crystallite-size and band-gap of TiO_2 NPs are found to be respectively 10 nm and 3.33 eV. The Ag-sensitized TiO_2films demonstrates good sensitivity towards chlorine (Cl_2) gas with response of ~110 % at 250 °C operating temperature with response time of 50 s for 100 ppm concentration. The Cl_2 gas sensing properties are investigated for lower range 5 ppm to higher range 400 ppm. In further studies responses of TiO_2 as function of operating temperature and gas concentration are explored in addition to repeatability and stability measurements.

KEYWORDS: Bio-synthesis, Ag-sensitized TiO_2, Cl_2 sensor, Sensitivity, Selectivity.

INTRODUCTION

The wide band gap semiconductor metal oxides are very useful for number applications: such as water purification, biomedical, solar cells, chemical and biological sensors and so on [1-6]. The semiconducting metal oxides [7 - 11] are found to be useful forfabrications of solid-state sensors due to their eco-friendly nature, low-costs, compatibility, availability in different dimensions, and low-power consumption methods. The fast response, low working temperature and good selectivity etc. are the main requirements of the good sensor. Further, to monitor the environmental gas presence, a very fast response of the sensor is required. However, the high operating temperature metal oxide-based gas sensors can lead ignition of fire related accidents and also they consume more energy. They show the sensing responses to the number of gases in the same temperature window. Hence, the development of sensor with low operating temperature, better sensing response and high selectivity to particular gas is an area of research interest.

The chlorine (Cl_2) is one of the poisonous gases,highly irritating, extremely reactive, destructive to living tissues and potentially lethal. Hence, the development of sensor for Cl_2 detection is very important. The non-toxic, abundantly available, cheap with excellent electrical and optical properties TiO_2 is not used very much for detection of different gases [12]. The wide-band gap *n*-type semiconducting TiO_2 is a promising material for number of applications such as solar cells, self-cleaning glasses, water purification, biological activities like anti-fungal [13]. It is reported that gas sensing properties of semiconducting metal oxide can be improved in terms of better sensitivity, low-operating temperature,fast response, and good selectivity by sensitizing them with noble metal nanoparticles [14-22].

Different methods [12, 23-27] are established for synthesis of TiO_2 active material. However, biological methods [25-27] are reported to be very useful because of their inherent properties like eco-friendly nature, low temperature processing, cost-effective,free from chemical reactions and zero production of hazardous waste as by-products.

In view of this, in present work,an attempt is made to prepare TiO_2nanoparticles (NPs) by using biological method. Further, the sensing response of silver (Ag) -sensitized TiO_2 films is also investigated for the different gases: NH_3, H_2S, CO_2, NO_2 and Cl_2. For this purpose, the TiO_2 films are made from bio-inspired TiO_2 NPs by using Doctor Blade method. Further, TiO_2 films are sensitized with Ag by using the dip coating technique. As-prepared TiO_2 NPs are characterized by using the different techniques: XRD, FESEM and UV-Visible spectroscopy. The gas sensing response of (Ag) -sensitized TiO_2 films were studied by using home-built static gas characterization system. The results pertaining to characterization of bio-synthesized TiO_2nanoparticles and NH_3, H_2S, CO_2, NO_2& Cl_2 sensing characteristics of Ag-sensitized TiO_2 film are presented in this paper.

EXPERIMENTAL

The TiO_2 nanoparticles (NPs)were prepared by using biosynthesis method [27]. Initially,*Ganoderma*mushroom fine powder was boiled in 100 ml double distilled water (DDW) at 85 °C for 15 min to prepare an extract of mushroom. The extract was filtered and then stored as a stock solution at 4 °C. The 0.15 M solution of titanium tetraisopropoxide (TTIP)wasprepared in ethyl alcohol. The 5 ml of mushroom extract was drop-wise added into 50 ml solution of TTIP. The precipitate obtained was dried and then annealed at 450 °C for 2 h to obtain TiO_2 powder. The glass substrates (size = 2 cm x 6 cm) were used for the preparation of sensor films of as-annealed TiO_2 powder by using doctor-blade method. The glass substrates were cleaned by using soap solution and then ultrasonicatedin deionized water and ethanol. The sensor film was prepared on cleaned glass substrate by using 0.1 gm/ml concentration of TiO_2 powder in deionized water in the presence of polyvinyl alcohol as a binder. This film was then air-annealed at 200 °C for 2 h to remove binder.

The silver nitrate ($AgNO_3$) was used as metal salt for the sensitization. The TiO_2 film prepared by using Doctor's Blade method was dipped in 10 mM aqueous solution of $AgNO_3$for 5 sec. and then dried under IR lamp. The 10 such cycles of dipping were carried out for film. The sensitized TiO_2 filmwas then heated at 200 ^{o}C for 1 hr to remove the nitrate from the deposit.The material characterizations of resultant

TiO_2 film was done by using different techniques: X-ray diffraction, field emission scanning electron microscopy and UV-Visible spectroscopy. The commercial silver paste was used to give two silver contacts at 10 mm apart from each other on the top surface of sensor film. Thegas sensing properties were measured by using the static gas sensing system. For this purpose, sensor film was mounted onto a heating plate in a sealed chamber and measured stabilized resistances (R_a) in the air and (R_g) in the presence of target gas. The gas response was obtained by using the relation:

$$S\,(\%) = \frac{|R_a - R_g|}{R_a}\, x\, 100 \qquad (1)$$

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) pattern of pure TiO_2film. The presenceof diffraction peaks in XRD pattern confirms the polycrystalline nature of the in resultant film. All diffraction peaks are matching with the reflections corresponding to anatasecubic phase (JCPDS card no. 21-1272) [5, 24, 27] of TiO_2. The occurrence of broad diffraction peaks with no impurity peaks indicates the formation nanocrystalline pure TiO_2 particles.The average value of crystallite size obtained from all diffraction peaks by using Scherrer's relation is found to be of 10 nm.

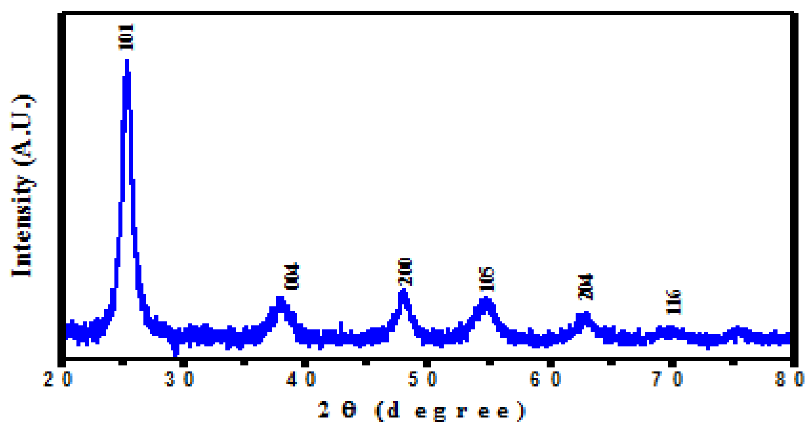


Figure 1: The X-ray diffraction (XRD) pattern of pureTiO_2 film

The field emission scanning electron micrograph (FESEM) of Ag - sensitized TiO_2 film is as shown in figure 2. The FESEM image confirms spherical nanoparticles (NPs)-like morphology of as-prepared TiO_2. The liquid sintering is observed at some part of the material. The average particle is noted to be 50 nm. The size distribution of TiO_2 NPs is observed to be nearly uniform. The energy dispersive spectrum (EDS) of Ag - sensitized TiO_2 film surface showed the presence of peaks corresponding to only Ag, Ti and O. It confirms the purity of resultant films.

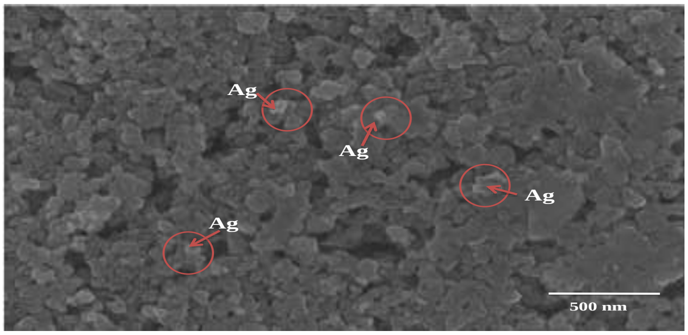


Figure2: Field emission scanning electron micrograph (FESEM) of Ag - sensitized film

The optical properties of pure TiO_2 film were investigated by using UV-Visible spectroscopy. Figure 3 shows UV-visible spectrum of TiO_2film. The UV absorbance peak was observed in ultra-violet region. The Tauc's relation of photon energy (hν) with absorption coefficient (α) is given as [3] in relation:

$$\alpha = \frac{\alpha_0 (h\nu - E_g)^n}{h\nu} \quad (2)$$

where, E_g = band gap energy, α = absorption coefficient, α_o= constant.The value of 'n' depends on the type of transition. The 'n' has values ½ and 2. The Tauc plot is shown as an inset of figure 3. The value of band gap is obtained by extrapolation of straight-line portion of the plot to zero absorption edge. The optical band gap energy of TiO_2 NPs film obtained from Tauc plot is found to be 3.33 eV.

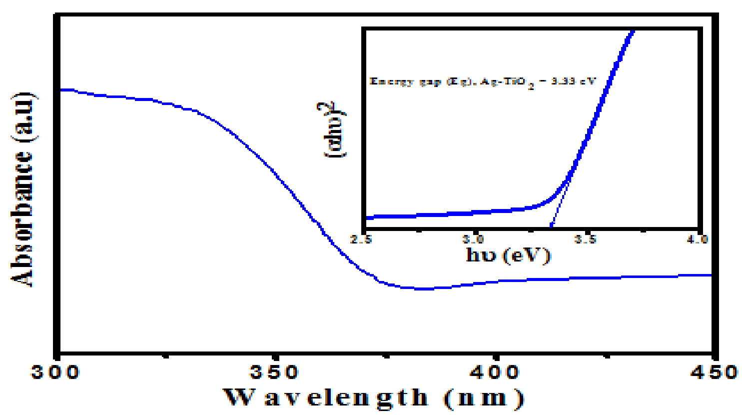


Figure 3: UV-visible spectrum of pure TiO_2 film (inset: Tauc plot: variation of $(\alpha h\nu)^2$ versus photon energy, hν(eV))

The gas sensing properties ofAg - sensitized TiO_2film were investigated by using home-built static gas sensing system. Figure 4 shows gas sensing response of the Ag - sensitized TiO_2 film for Cl_2target gas (with concentration ~100 ppm) at various operating temperatures. The highest Cl_2 gas response of 110.1 % at 250 °C operating temperature is observed for Ag - sensitized TiO_2 film. The*n*-type semiconducting behavior of TiO_2 is due to the defects arising from oxygen vacancies. The change in the resistance in the presence of test gas is the basis for working of sensor. It is found that the resistance of TiO_2 film increases on exposure of Cl_2 test gas. A typical Cl_2 gas sensing mechanism for '*n*' type metal oxide semiconductor gas sensor has been explained by Navale et al. [28].

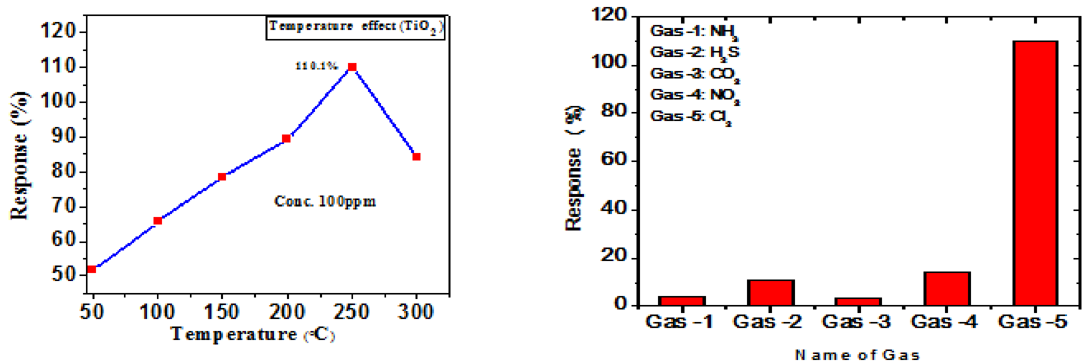
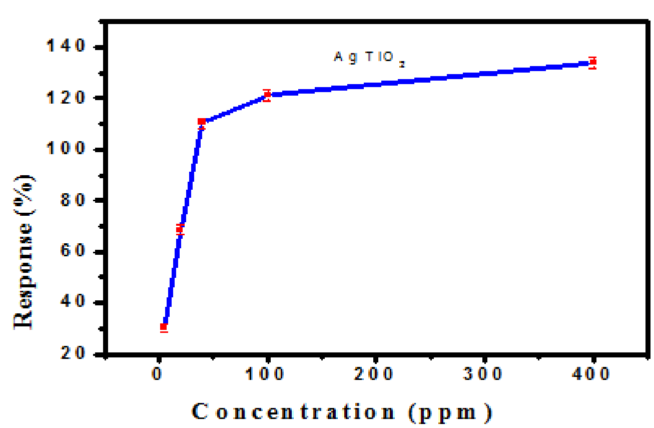


Figure 4: The variation of sensor response at different operating temperatures for Ag - sensitized TiO_2 film at 100 ppm of Cl_2 target gas (Left) and sensor response for Ag - sensitized TiO_2film at 100 ppm for different test gases (right).

The sensing response of Ag -sensitized TiO_2 film is also measured at 100 ppm concentrations of different gases: NH_3, H_2S, CO_2, andNO_2. Figure 4 (bottom) gives the sensing response of Ag -sensitized TiO_2 film at 100 ppm for different test gases: NH_3, H_2S, CO_2, NO_2 and Cl_2. The highest sensing response is noted for the Cl_2 gas as compared to other gases: NH_3, H_2S, CO_2, and NO_2. It indicates that Ag-sensitized TiO_2 film is having good selectivity towards Cl_2 gas. On exposure of Ag - sensitized TiO_2sensor film to the test gas, the sensor response is increasing till saturation or equilibrium level for given concentration of target gas is achieved. At saturation level, sensor film shows constant response.



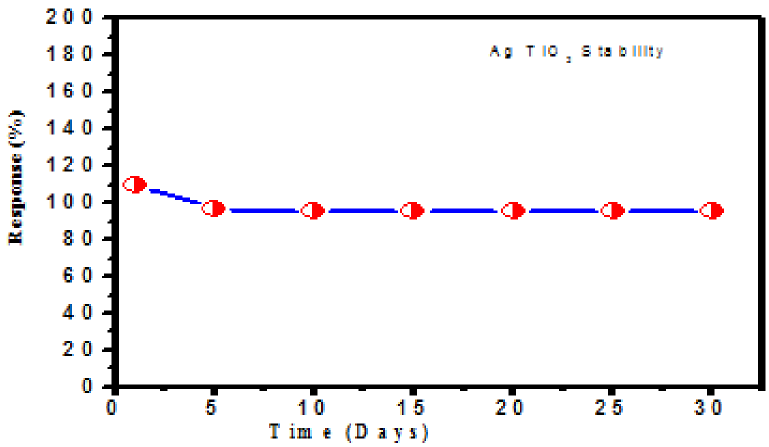


Figure 5: Variation sensor response at different concentration (ppm) of Cl_2 target gas (top) and variation of sensor response at 100 ppm of Cl_2 target gas on different day (bottom) for Ag - sensitized TiO_2film

After exposure of Ag -sensitized TiO_2 film to an external atmosphere, the target gas molecules start desorbing and corresponding sensor response also decreases. The response time: time taken by Ag-sensitized TiO_2 film to reach 90% of change in resistance value for given 100 ppm concentration of Cl_2gas is recorded to be 50 s. The recovery time value for Ag - sensitized TiO_2 film is found to be 52 s. Thus Cl_2 detection sensing response by Ag - sensitized TiO_2 film is fast. Figure 5 (top) gives the variation of sensor response at different concentration (ppm) of Cl_2 target gasfor Ag -sensitized TiO_2film. It is observed that the sensor shows lower gas response for low concentration of Cl_2 gas. As concentration of Cl_2increases the corresponding response is also increased.The stability of Ag -sensitized TiO_2 film sensor was confirmed after periodic time interval. Figure 5 (bottom) gives the variation of sensor response at 100 ppm concentration of Cl_2 target gas on different days for Ag -sensitized TiO_2 film. The Ag -sensitized TiO_2 film sensor shows good stability towards the Cl_2 gas sensing.

CONCLUSION

In summary, bio-synthesis is economical method and is easy way for preparation of TiO_2 required for developing gas sensor. The Ag -sensitized TiO_2 filmsensor shows good selectivity towards Cl_2 gas sensing. It shows highest Cl_2 gas response of 110.1 % for 100 ppm at 250 °C operating temperature. The response and recovery times for this sensor are found to be 50 s and 52 s respectively. The Ag -sensitized TiO_2 filmsensoralso shows good repeatability and stability for Cl_2gas sensing.

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