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DEVELOPEMENT OF AMMONIA SENSOR USING NANO-TITANIUM BLENDED HYDROXYAPATITE NANOCERAMICS

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Abstract: Ammonia gas sensing study of nano Titanium dioxide (TiO_2) blended nano Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$) (HAp) is carried out by two probe methods. The composites are made by mechanical blending in different proportion such as 1% TiO_2 , 2% TiO_2 , and 5% TiO_2 in HAp matrix. Thick films of blended composites are prepared by standard screen printing technique. These films are dried at 600 °C for 1 hour in air atmosphere. The surface topography of HAp is observed by atomic force microscopy (AFM) technique while crystal and size is estimated by X-ray diffraction technique (XRD). FTIR is performed to confirm functional groups. The thermal analysis is carried out by means of TG/DTA to assess phase changes in TiO_2 mixed HAp composites. The sensor substrates are developed for sensing ammonia gas at various concentrations as well as at various temperatures. It is observed that the operating temperature for ammonia sensing is found to be as low as 25 degree C. The response and recovery capabilities of such films are seen for varied ammonia concentrations from the point of view of using these sensors as a commercial ammonia sensor device. It is concluded that Ti based Hap matrix are one of the unique rugged ammonia sensors at room temperature as observed experimentally from their large number of gas uptake/recovery cycles.

Keywords: Titanium dioxide (TiO_2), Hydroxyapatite, Ammonia (NH_3)

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INTRODUCTION

Ammonia, a compound of nitrogen and hydrogen, is a colourless gas with a characteristic pungent smell and widely used in various areas such as food, fertilizers, pharmaceutical industries, for refrigeration system and in laboratory as analytical reagent^[1]. Since ammonia is irritating and corrosive, its exposure at high concentrations in air causes immediate burning of the nose, throat and respiratory tract. This can cause bronchiolar and alveolar edema. Inhalation of lower concentrations can cause coughing and nose/throat/skin/eye irritation. Contact with concentrated ammonia solutions such as industrial cleaners may cause corrosive injury including skin burns, permanent eye damage or blindness^[2].

Hydroxyapatite (HAp) is naturally occurring mineral having chemical formula $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$, and is widely utilised because of its adsorption affinity, biocompatibility, low water solubility, high stability^[3-6]. These Properties of HAp can be useful for the purpose of gas sensing. Moreover, nanosized TiO_2 when blended with HAp can enhance gas sensing properties, since TiO_2 is known to be a good gas sensor besides having properties like photocatalysis and physicochemical stability.

MATERIALS AND METHODS

HAp material is synthesized by wet chemical method as described in our previous work^[3-6]. Nanosized TiO_2 is synthesized by sol-gel method^[7]. TiO_2 -HAp blending is done by mechanical mixing of 1%, 2% and 5% TiO_2 in HAp powder. Thick films of such blended materials are prepared by standard screen printing method. The blends are characterized by XRD, FTIR, and TG/DTA. The gas sensing performance of pure TiO_2 , pure HAp and TiO_2 blended HAp is measured in a specially designed experimental set up described earlier, by two probe electrical method.

RESULTS AND DISCUSSION:

X-Ray Diffraction analysis (XRD)

Figure 1 shows the XRD pattern of pure TiO_2 , pure HAp and TiO_2 , blended HAp. The XRD pattern in figure 1(A) shows the characteristics peaks at 2θ values of 25° , 37° , 48° , 54° , 55° and 62° , which corresponds to crystal plane (101), (004), (200), (105), (211), (204) respectively. It clearly shows the synthesized TiO_2 in crystalline form having Anatase phase of TiO_2 [1, 5]. Figure 1(B) shows the peak at 2θ values 25.6° , 26.4° , 30.1° , 31.7° , 32.7° , 35.1° , 36.1° , 40.1° , 43.3° , 52.5° corresponding to (201), (002), (102), (211), (300), (301), (221), (213), and (303) crystalline planes respectively, indicating

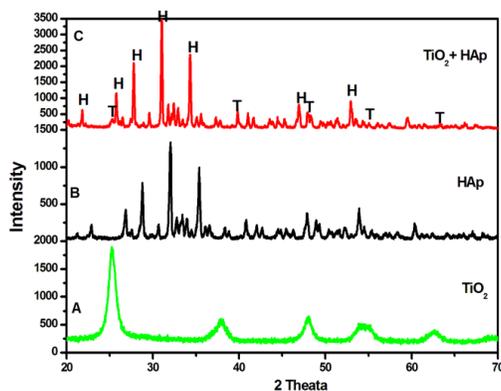


Fig.1 XRD pattern (A) Pure TiO_2 , (B) pure HAp, (C) TiO_2 blended HAp.

standard hexagonal phase structure of HAp.^[3-9] XRD analysis of TiO_2 blended HAp gives the characteristic peaks for both TiO_2 as well as for HAp which is indicated by letter T and H respectively^[10].

Thermal gravimetric differential thermal analysis (TG/DTA)

The thermal properties of TiO_2 , and HAp, are carried out by TG/DTA by heating the material from 30°C to 1000°C . The TG/DTA curve obtained for TiO_2 and for HAp is shown in figure 2(A) and 2(B) respectively. The TGA curve for pure TiO_2 shows no change from the 30°C - 100°C but above 100°C , the curve shows decrease in mass from 13.73 mg to 10.22 mg. This loss in weight is due to removal of water and OH group from TiO_2 . This change is observed in the temperature region from 110 to 500°C ^[11]. After 500°C , the curve remains flat up to 1000°C which indicates the phase transformation from anatase to stable Rutile phase^[9, 11]. The DTA curve of pure TiO_2 shows the endothermic peak at 135°C , which is due to desorption of adsorbed water.

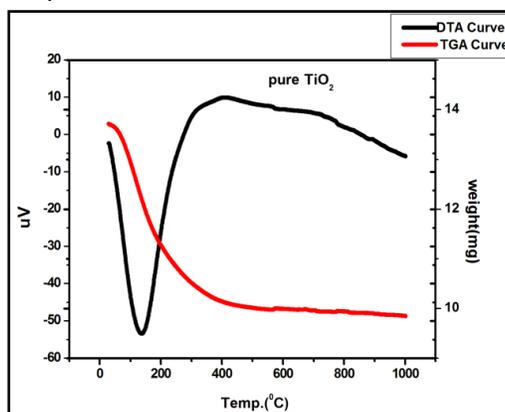


Fig.2 A .TG/DTA curve of pure TiO_2

Fig. 2 B depicts that pure form of Hap is thermally stable material.^[13]

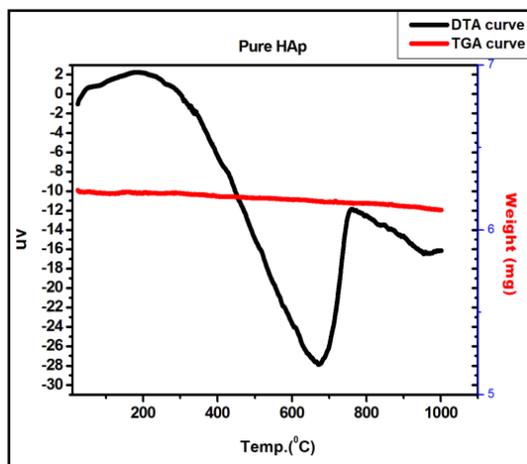


Fig.2 B. TG/DTA curve of pure HAp

Fourier transforms infrared spectroscopy (FTIR).

FTIR spectra of pure TiO_2 , pure HAp and TiO_2 blended HAp recorded at room temperature in the range of wave number $4000\text{-}400\text{ cm}^{-1}$ are shown in a figure 3. The spectra (A) shows the presence of two characteristics small bands at 550 cm^{-1} , and 607 cm^{-1} , possibly due to the vibration of the Ti—O bonds in the TiO_2 lattice [7]. The broad spectra at $1620\text{-}1630\text{ cm}^{-1}$ are assigned to vibrations of hydroxyl groups [3]. The peaks appeared at 2847 cm^{-1} , 2925 cm^{-1} are attributed to CH_2 group in prevailing in the starting composition $\text{TiCl}_4(\text{OC}_2\text{H}_5)$ [7].

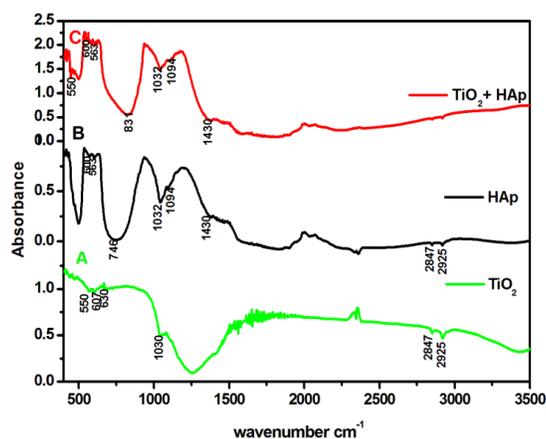


Fig.3 (A-C) FTIR Spectra of: (A) Pure TiO_2 , (B) pure HAp, (C) TiO_2 blended HAp.

A weak peak at 630 cm^{-1} belongs to vibrations of Ti-O-C bond [4, 12]. The spectra B is for pure HAp, wherein the peaks at 1032 cm^{-1} , 1094 cm^{-1} , 600 cm^{-1} and 563 cm^{-1} are assigned as the stretching and bending modes of phosphate (PO_4) of HAp [3]. Small band at 741 cm^{-1}

corresponds to the stretching mode of hydroxyl group of HAp^[3]. All characteristic peaks of TiO₂ blended HAp can be observed in spectra (C).

Gas sensing performance

Operating temperature

Fig. 4 shows the behaviour of resistance of thick films of pure TiO₂, pure HAp and TiO₂ blended HAp for 50 ppm Ammonia gas for various temperatures.

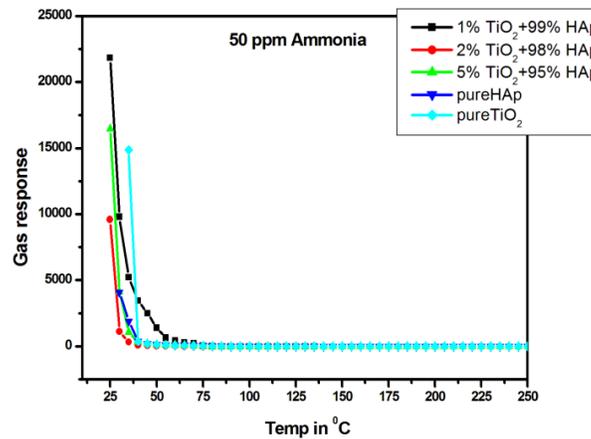


Fig.4 variation of gas response with temperature

To determine the operating temperature, two probe electrical methods is adopted as discussed in detail in our previous work^[3-6, 13]. It is observed that the sensor substrate shows increasing gas response at lower temperature as seen from fig.4. It is observed that the maximum gas response for pure TiO₂ as well as for pure HAp at 30 °C, while that for TiO₂ blended Hap is obtained at 25 °C, showing such blended sensors can be operated at room temperatures.

Determination of response and recovery time

Figure 5 shows the variation in resistance of sensor material at temperature of 25°C as a function of time, in presence of fixed concentration of ammonia gas.

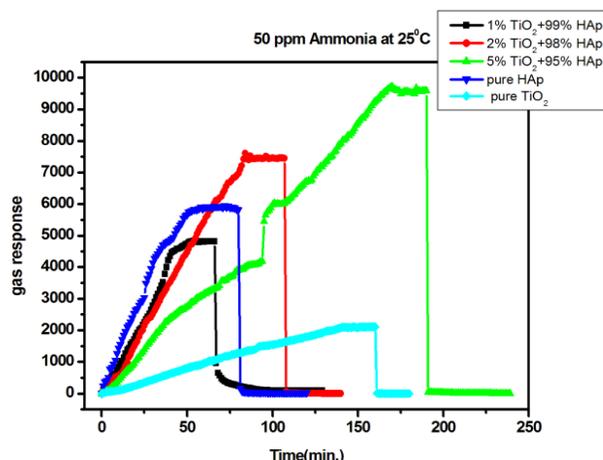


Fig 5. Response and Recovery time for pure TiO₂, pure HAp and for TiO₂ blended HAp at 25 °C for 50 ppm ammonia.

After injection of test gas (50 ppm ammonia), the resistance of sensor material is increased slowly with respect to increase in time due to interaction of gas with the sensor material. The time at which the gas shows maximum response to test gas is considered to be response time of sensor substrate. Upon exposing the sensor material to atmospheric air, the resistance reverts back to its original value. Thus the time required for sensor material to revert its original value is termed as recovery time. The value of response and recovery time is observed to depend on the substrate composition respectively, as written in the brackets, e.g., Pure TiO₂ (120 min and 2 min), Pure Hap(51 min and just 1 min, for 1% TiO₂ blended HAp 30 min and 25 sec., for 2% TiO₂ in HAp 82 minute and 30 sec and for 5% TiO₂ in 95% 165 min and 2 min respectively. Hence although the sensitivity is little less, 1% TiO₂-Hap films are useful for rapid sensing.

Determination Gas uptake capacity

For determination of gas uptake capacity of sensor material, the thick films of sensing material are exposed to various concentration level of ammonia gas at their respective operating temperatures.

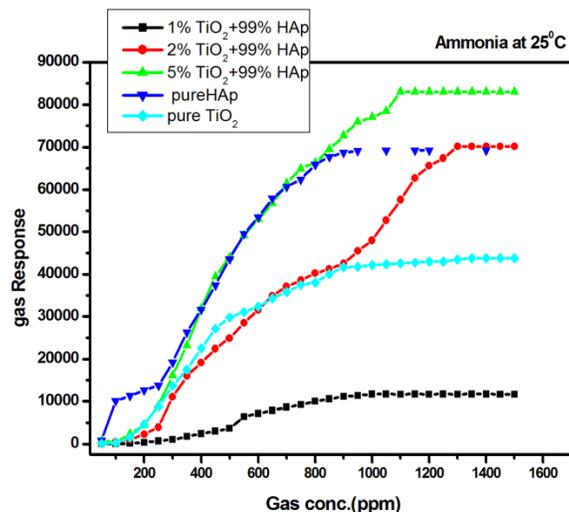


Fig.6. Variation of gas response with ammonia concentration for pure TiO₂, pure HAp, and for TiO₂ blended HAp.

Figure 6 shows the gas uptake capacity for various TiO₂-HAp sensor substrates. Initially, for almost all sensors, the gas response increases with increase in gas concentration, later achieving a constant value, termed as saturation value or maximum gas uptake. The maximum gas uptake of 1000ppm ammonia is seen to achieve by blending 5% TiO₂ in HAp.

CONCLUSION

In this work, the ammonia gas sensing performance is shown to be enhanced by blending TiO₂ in HAp matrix, with rapid gas response and regenerative sensor capabilities. It is concluded that 1% TiO₂ blended HAp can be used for smart sensing at low ppm concentrations of ammonia while for larger ammonia gas loads, 5% TiO₂ blended HAp can be utilised for commercial applications substrates for ammonia sensor devices.

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