

Application of TiO₂/SnO₂ nanoparticles in photoluminescence based fast ammonia gas sensing

Nitu Singh¹ · Vinita Pandey¹ · Neha Singh¹ · M. M. Malik¹ · Fozia Z. Haque¹

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Abstract In the present research work we reported the highly dispersible TiO₂/SnO₂ nanoparticles produced via a simple aqueous solution growth technique with ~50 nm average grain size. The surface morphology of the material have been studied by using scanning electron (SEM) and atomic force microscopes (AFM). Using photoluminescence, interaction between ammonia gas and TiO₂/SnO₂ (60:40 composition) nanoparticles were investigated. The material shows average significant increment in the PL intensity with no shifting in peak, which conform its tremendous applicability in optical gas sensor to detect ammonia gas (20 ppm) using photoluminescence technique. The gas sensing was systematically performed through photoluminescence spectrometer for different concentration of ammonia at room temperature. The response and recovery time of these samples are found to be in the range of 12 and 50 s respectively.

Keywords TiO₂/SnO₂ nanoparticles · Atomic force microscopy · Scanning electron microscope · Photoluminescence · Response time · Ammonia gas

Introduction

The TiO₂ and SnO₂ are N-type semiconducting metal oxide gas sensors. They are currently constitute one of the most investigated groups of gas sensors. TiO₂ and SnO₂ and

some other oxide nanoparticles nanomaterial have attracted much attention due to their unique optical, dielectric and mechanical properties as well as numerous potential applications including photo catalysis, optical coating, and photoelectron chemical solar cells [1–6]. They have attracted much attention in the field of gas sensing under atmospheric conditions due to their low cost and flexibility in production; simplicity of their use; large number of detectable gases is possible. In addition to the radiative property changes of gas-sensing material, the detection of this reaction can be performed by measuring the change of optical characteristics, work function, capacitance, mass or reaction energy released by the gas/solid interaction [2–6]. The main attention in this paper will be focused on the optical characteristics of the TiO₂/SnO₂ semiconducting metal oxide for gas sensors. Photoluminescence spectroscopy as an important tool has been used to study TiO₂/SnO₂ sensing of gas.

There are various chemical methods for the synthesis of ultrafine oxide nanoparticles such as sol–gel, hydrothermal, aqueous solution growth technique flame combustion and precipitation. The aqueous solution growth technique is one of the best methods for fabricate material at low cost with mild temperatures, high purity materials with control in the nanostructure and surface properties. The synthesis involves the controlled heteronucleation of metal oxides in aqueous solutions [7–9]. Single-crystal nanostructures can give rise to novel useful properties in different application fields, such as gas sensing. Indeed, the average surface-to-volume ratio, consequent on the reduced sized of nanostructures leads to an enhanced surface interaction [10–15]. In particular, sensors based on the variations of the photoluminescence (PL) emission in the presence/absence of gas molecules are attractive because they can provide high responses at room temperature and result stable with a

✉ Fozia Z. Haque
foziazia@rediffmail.com

¹ Optical Nanomaterials Lab, Department of Physics, Maulana Azad National Institute of Technology, Bhopa, MP 462051, India

rapid, reproducible and good sensitivity [16]. $\text{TiO}_2/\text{SnO}_2$ nanoparticles can also be produced by a variety of techniques ranging from simple chemical to mechanical to vacuum methods, including many variants of physical and chemical vapour deposition techniques for using as gas sensing elements [16–18].

A sensor is defined as a device able to convert a chemical or physical variation to be monitored into an easily processable signal. The sensing element (material) has to fulfill essentially two different tasks: first, it has to interact with the target gas through various mechanisms like surface adsorption, charge transfer, ionic exchange then this interaction has to be transformed into an easily processable signal, like a change in electrical conductivity or in optical properties. Particularly in metal oxides and carbon nanotubes, the mechanisms for recognizing the gases to be determined include absorption processes. There is a variety of sensing devices that rely on different chemical or physical phenomena: in fact the analyte presence can be detected through changes in electrical properties (conductivity, impedance, capacitance), optical properties (absorption, reflection, luminescence, refractive index) or other physical properties (mass, thermal conductivity, acoustic waves propagation), measuring the reaction heat analyzing specific electrochemical or biochemical recognition, and so on. The first and at the moment more established sensors are based on a conductometric interface: historically the birth of electrical sensor is dated 1962, when SnO_2 has been assessed as good material for gas detection [19–24]. All the electrical sensors have limitation like contact problem and selectivity of gases but this problem can be solved through optical/Luminescent sensor.

In present work, $\text{TiO}_2/\text{SnO}_2$ nanoparticle are prepared via simple aqueous solution growth technique which is assisted by ultrasonication and characterization of prepared TiO_2 is done by SEM and AFM. The optical and sensing properties were studied through photoluminescence (PL) spectra at room temperature and the data were recorded using fluorescence spectrometer (F-7000 Hitachi) exciting with its Xenon lamp at 242 nm. All the reagent used were of analytical grade and no further purification was done.

Experimental procedure

Reagent

Tetraisopropoxide (purity, 97%), Ti $[\text{OC}_3\text{H}_7]_4$ and $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ were used as a starting material and supplied by sigma-Aldrich company. Ethanol $[\text{C}_2\text{H}_6\text{O}]$ and nitric acid $[\text{HNO}_3]$ from Merck. Distilled water was used for

preparing all standard solutions. The chemicals were used without any further purification.

Synthesis process

In this research paper, $\text{TiO}_2/\text{SnO}_2$ nanoparticle in the composition of 60:40 are prepared via simple aqueous solution growth technique which is assisted by ultrasonication. The aqueous solution synthesized $\text{TiO}_2/\text{SnO}_2$ was obtained from 0.1 M titanium(IV) Isopropoxide (TTIP) and 1.5 mg $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 75 ml absolute ethanol and distilled water was added to the solution in terms of a molar ratio $\text{Ti}:\text{Sn}:\text{H}_2\text{O} = 0.6:0.4:4$. Nitric acid was used to adjust the pH and for restrain the process of the solution. The solution was vigorously stirred for 30 min. After ageing 24 h, it transformed into precipitate. In order to obtain nanoparticle, the precipitate was dried under 90–100 °C for 3 h to evaporate water and organic material to the maximum extent. Then the dry precipitate was sintered at 450 °C for 4 h were subsequently carried out to obtain $\text{TiO}_2/\text{SnO}_2$ powder.

Gas sensing measurement

For optical gas sensing measurement, the sample was excited by a Xenon laser as light source [F-7000 Hitachi] at 242 nm excitation wavelength. PL spectra were acquired perpendicular to the sample surface using a single spectrograph. A filter was used to filter out secondary wavelength during the whole measurements. A sample holder is designed in lab to study the effect of gas on Photoluminescence of materials in situ. This sample holder is made from quartz tube with a cuvette vertically attached in its bottom. Sample was placed inside the cuvette of quartz sample holder at room temperature; this sample holder was kept inside the spectrometer chamber for optical measurements. The data is recorded in the presence of simple air in chamber then the sample holder was filled with 20 ppm ammonia gas and data was again recorded after the exposure for comparison.

Characterization

Scanning Electron Microscopy (SEM, JEOL-JSM-6390) and Atomic Force Microscopy (AFM), NT-MDT Solver NEXT, was used to define the morphology chemical composition of as prepared samples. Optical properties and gas sensing were studied through Photoluminescence (PL) spectra at room temperature and the data were recorded using fluorescence spectrometer (F-7000 Hitachi) exciting with its xenon lamp at 242 nm.

Surface morphology

For investigating the morphology of the synthesized TiO₂ nanoparticle SEM and AFM were used. The SEM images are shown in Fig. 1 and AFM images are shown in Fig. 2 (a, b) on the scale of 200 nm.

Both SEM and AFM provides extraordinary topographic contrast and unobscured views of surface features. To analyze surface morphology, the 1 × 1 μm image was taken from the sample using an Atomic Force Microscope (AFM). Two-dimensional image and average grain size and average diameter of the sample is shown in Fig. 2b. From this image, it can be seen that dispersion of ZnO nanoparticles is relatively uniform. Average grain size and diameter of particle were determined with the help of Nova PX analysis software programming.

The average crystallite size of the ZnO sample was found to be 50 nm, the average aspect ratio is 26, average particle size is 60 nm. As seen in AFM images, the ZnO sample was formed from the particles like circles which are in good agreement with SEM results. The particles are well distributed in the sample and the average roughness of sample was estimated as 1.62 nm using Nova PX software.

Photoluminescence and gas sensing study

Photoluminescence (PL) is a non-destructive technique used for the investigation of extrinsic and intrinsic properties of semiconductors. In this technique the semiconductor under investigation is excited optically and then the PL spectrum of the spontaneous emission from radiative recombination in the semiconductor band gap is obtained. During the PL process both radiative and non radiative recombination happen. The PL technique can be used to determine the bandgap, impurity levels, defects detection and recombination process in the semiconductor materials.

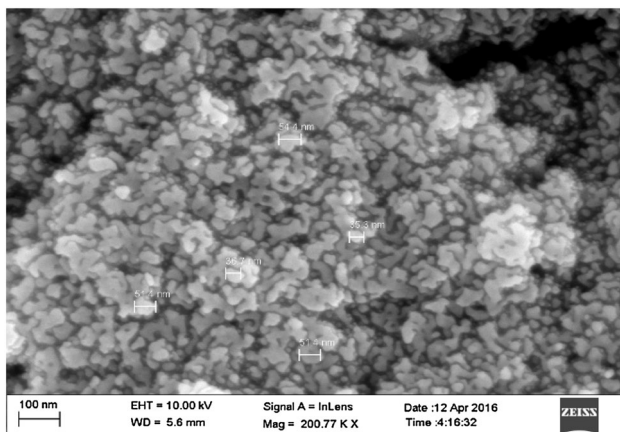


Fig. 1 SEM image of TiO₂/SnO₂ nanoparticles

A Photoluminescence excitation spectrum is shown in Fig. 3. When the material is excited at 242 nm in the absence of ammonia gas, a strong emission peaks were observed around 422 nm due to violet emission which is attributed to the recombination of an electron and hole in the valance band. The second peak were observed at 465 nm (2.72 eV) due to blue emission. The blue emission might be related to the surface defect and confine particle size in TiO₂/SnO₂ thin film. The other two peak were observed at 512.4 and 545.4 nm (green emission). Due to oxygen vacancies and recombination of electron, oxygen vacancies occur in three different charge states, the neutral oxygen vacancy, the singly ionized oxygen vacancy and doubly ionized oxygen vacancy, only the singly ionized oxygen vacancy can act as the luminescent center, green emission decreased mainly due to decrease in the oxygen vacancies in the samples. When TiO₂/SnO₂ nanoparticle is again excited at 242 nm in the presence of 20 ppm ammonia gas, a strong emission peak is observed at same wavelength but this time the intensity of the peak increased due to ammonia gas which is reducing in nature [25–27]. The overlay plot of TiO₂/SnO₂ in presence of ammonia and in the absence of ammonia is given in Fig. 3.

Time response

Time response graph plotted between intensity and time for TiO₂/SnO₂ is shown in Fig. 4, and the curve is following a step change in composition from air to 20 ppm NH₃ to again air at the room temperature. The response and recovery time are determined from this plot.

It is observed that when gas enter into the chamber it react with the oxygen present at the surface of TiO₂/SnO₂ due to which the radiative property of the TiO₂/SnO₂ start increasing and the intensity goes to its maximum and becomes constant in saturation state.

The response time (rise time) represents the time required by the sensitivity factor to undergo 90% variation with respect to its equilibrium value following a step increase in the test gas concentration and it was found to be 12 s in this case. Similarly, the recovery time (settling time) represents the time required by the sensitivity factor to return to 10% below its equilibrium value in air following the zeroing of the test gas ammonia and it was found to be around 50 s.

Sensing mechanism

TiO₂/SnO₂ is an n-type semiconductor where the majority charge carriers are electrons, and upon interaction with a reducing gas an increase in radiative property of material can occurs. Conversely, an oxidizing gas serves to deplete the sensing layer of charge carrying electrons, resulting in a

Fig. 2 a 2D image and b Histogram of TiO₂/SnO₂ nanoparticles from AFM study

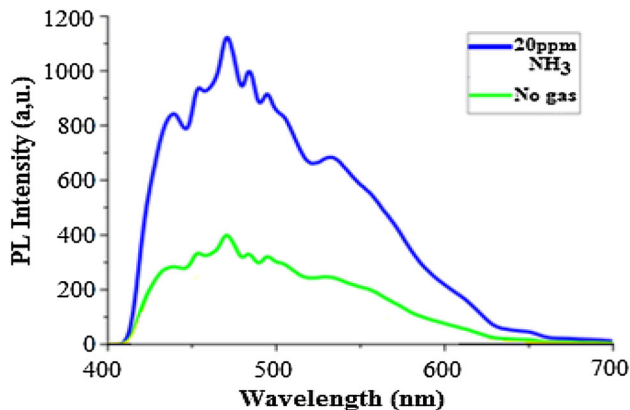
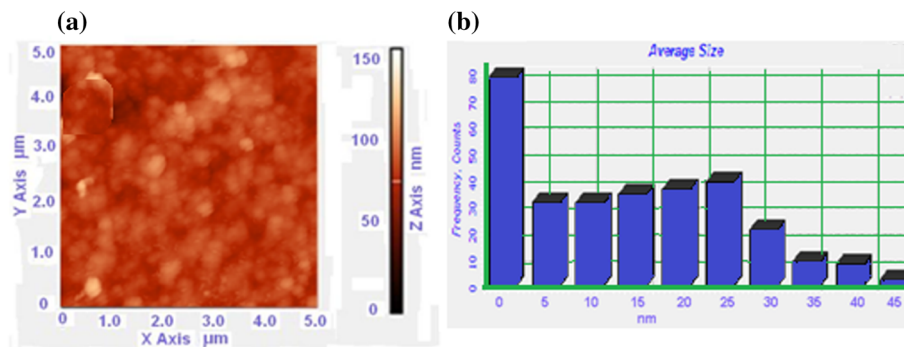


Fig. 3 PL overlay plot of TiO₂/SnO₂ nanoparticles in the air and in the presence of ammonia

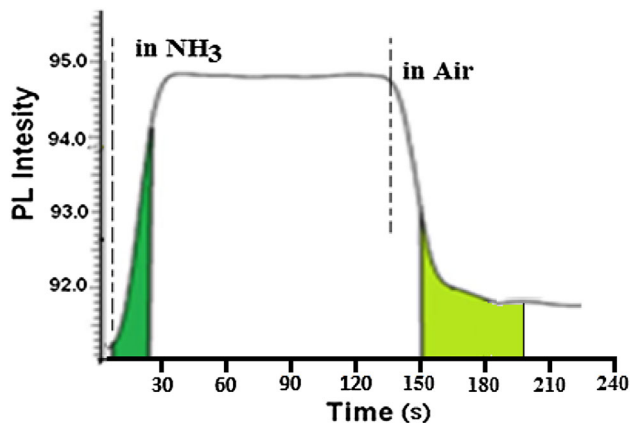


Fig. 4 Response time of TiO₂/SnO₂ Nanoparticles for 20 ppm NH₃ gas

decrease in radiative property. A p-type semiconductor is a material where the majority charge carriers are holes (Table 1) hence, the opposite effects are observed with the material and showing an decrease in the radiative property of material in the presence of an reducing gas. When O₂ molecules are adsorbed on the surface of TiO₂/SnO₂, they would extract electrons from the conduction band E_c and trap electrons at the surface in the form of ions. This will

Table 1 Charge carrier in different types of semiconductors

Classification	Radiative property	
	Oxidising gases	Reducing gases
n-type	Decrease	Increase
p-type	Increase	Decrease

lead a band bending and an electron depleted region. This electron depleted region is also known as space-charge layer, the thickness of which is the length of band bending region [28–31].

Reaction of these oxygen species with reducing gases or a competitive adsorption and replacement of the adsorbed oxygen by other molecules decreases and can reverse the band bending, resulting in an increased radiative property. In clean air the radiative property of TiO₂/SnO₂ is low because the conduction electrons are bound to surface oxygen, whereas in the presence of a reducing gas, electrons are no longer bound to the surface states and the radiative property increases. Therefore, the adsorption of gaseous species controls the surface radiative property of TiO₂/SnO₂ as well as that of grain boundaries.

Conclusion

The near spherical and well distributed TiO₂/SnO₂ nanoparticles have been synthesized using simple aqueous solution growth techniques from the solution TTIP and SnCl₂·6H₂O. The material show good Photoluminescence with a strong violet emission at around 420 nm. The material undergoes a significant increase in PL intensity upon exposure of ammonia and exhibits a fast response (12 s) and recovery time (50 s) at room temperature with only 20 ppm ammonia. These results shows good response of TiO₂/SnO₂ nanoparticles to be used as an analyte for Luminescence based ammonia gas sensor with fast response time. The mechanism of sensing gas by

measuring change in luminescent properties is very innovative and effective. This mechanism is efficient for fast sensing of very small fraction of gases.

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