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Green and Low-Cost Synthesis of TiO_2 Nanoparticles for Methanol Detection

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TiO_2 nanoparticles synthesis using *Ficus benghalensis* leaf extract *via* green synthesis approach, were characterized using XRD, FTIR, EDAX analysis and SEM. The present study explores the use of as-synthesized TiO_2 nanoparticles for the detection of methanol by spin-coating as-synthesized TiO_2 nanoparticles (~ 100 nm thickness) over n-type Si substrate as an active material with Au sputtered electrodes (~ 60 nm). The change in resistivity and electrical conductivity when exposed to the analyte clearly evidenced the detection at low operating temperature is recorded. The response curve of transient resistance *vs*. time was recorded at different working temperatures (50-200 ºC) and the device tested multiple times exhibited the same behaviour affirming the reproducibility with stability of thin film sensor is reported.

Keywords: *Ficus benghalensis* leaves, Green Synthesis, TiO_2 nanoparticles, Methanol.

INTRODUCTION

Nanomaterials generally exhibits remarkable properties in their respective field of applications, especially the considering the sensing applications semiconductors play vital role in the detection of various analytes [1-4]. The metal oxide semiconductors in their nanostructured showcase greater impact towards sensing ability in comparison with micro and macro-structured materials owing to their intrinsic and optimistic material characteristics. The blend approaches of nanotechnology and microelectronics have established their unique sway over high density structure, smart materials generation with innovative multi-analyte sensing devices for the raise in demand for highly sensitive and highly selective smart sensors with greater efficiency detecting multi-analytes in real-time applications [5-8]. However, the use of semiconducting metal oxide nanoparticles for gas sensing applications have been prominent source but using green synthesized nanoparticles has tremendous upsurge of interest in the recent past [9-11]. The researchers are much determined in using these green non-toxic nanoparticles in emerging technologies such as photonics, electronics, catalysts, sensing applications, micro and nano devices, *etc.* [12-15].

The TiO_2 nanoparticles is one among the most commonly used material for gas sensing applications with a wide band gap (3.2-3.35 eV) and large binding energy. TiO_2 nanoparticles is generally reviewed as the favourable resistive-type active media for sensing various gas molecules [16-18]. The gas molecules surface interactions onto the nanostructured metal oxides is normally the measure of charge density of charge carriers and conductance or resistance is measured to analyze the device sensing performance, which reprints the ability of semiconducting metal oxide nanoparticles. The TiO_2 nanostructure can be synthesized using various technique such as sol-gel method, hydrothermal synthesis technique, electro-anodization, chemical vapour technique, template assisted and physical vapour deposition technique [19-21]. The inalienable oxygen opening in TiO_2 species shows that there is more in addition to charge from Ti when contrasted with less oxygen charge. As affirmed from the stoichiometry hypothesis for semiconductor, this sort of rich electron and has a place with n-type semiconductor.

In present work, an easy, cost-effective and eco-friedly sustainable green approach is utilized for the synthesis of TiO_2 nanoparticles *via* aqueous extract of *Ficus benghalensis* leaves. The TiO_2 nanoparticles as-synthesized were obtained at much

ease of process. The as-synthesized nanoparticles first of its kind, were characterized using various analytical instruments such as X-ray diffraction (XRD), energy dispersive X-ray (EDAX) analysis, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy analysis. The TiO_2 nanoparticles were deposited over n-type Si substrate with gold (Au) sputtered as electrodes to measure the detctection of methanol and affirm the sensing studies with varying electrical parameters that ensures notable sensitivity and reproducibility. Present work reported the synthesis of TiO_2 nanoparticles, their characterization and the fabricated device sensing performance.

EXPERIMENTAL

The AR grade solvents such as ethanol and isopropyl alcohol (IPA) were procured from Merck, while titanium tetraisopropoxide (TTIP) was procured from Sigma-Aldrich, USA.

Extraction of aqueous *Ficus benghalensis* leaf: Initially, *Ficus benghalensis* fresh leaves collected from the local areas were rinsed and washed thoroughly with distilled water to remove any sort of dust cling to the surface. Furthermore, the leaves were allowed to dry at 60 ºC in a hot-air oven so that water droplets on surface dry completely. These dry leaves were grinded using lab grinder to obtain powder form of leaf which was collected and stored. *Ficus benghalensis* leaf extract was prepared by mixing 50 g of obtained leaf powder with 100 mL of distilled water, which is normally used as capping/stabilizing agent and the resultant mixture was annealed at 90 ºC for 45 min with continuous stirring at 400 rpm. The resultant solution was filtered using Whatman filter paper once after the annealing process. This extract was further used in the process of synthesis of TiO_2 nanoparticles.

Synthesis of TiO_2 nanoparticles: TiO_2 nanoparticles by the green/biogenic approach were prepared by adding 50 mL of 1M TTIP solution to 50 mL of *Ficus benghalensis* leaf extract in 1:1 ratio of (volume/volume) followed by continuous stirring at room temperature for 4 h. The technique involved in the formation of TiO_2 nanoparticles by hydrolysis of TTIP, which was the presiding pathway for obtaining the TiO_2 nanoparticles. The leaf extract present in resultant mixture act as a capping/stabilizing agent was to avoid agglomeration and to achieve the desired shape/size of the green TiO_2 nanoparticles. The resultant mixture was centrifuged at 5000 rpm for 10 min after the stirring process so that the precipitate is formed at bottom and these nanoparticles were collected. The collected wet TiO_2 nanoparticles were dried at 100 ºC for 12 h and then subjected to calcination at 500 ºC in a muffle furnace for 2 h. Thus, obtained green/biogenic synthesized TiO_2 nanoparticles were collected and stored for further characterization and use of this as-synthesized TiO_2 nanoparticles were spun on Si substrate to study detection of methanol.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis: The as-synthesized TiO_2 nanoparticles were recorded using XRD instrument at room temperature, alongside the angle of 20-80º (in 2θ range) using X-ray diffractometer (Rigaku Ultima IV instrument). The recorded XRD pattern of TiO_2 nanoparticles confirms that it belongs to the anatase phase, with tetragonal crystal system (Fig. 1). The TiO_2 nanoparticles characteristic peaks were observed angles from 0º to 70º at (2θ) of 25.43º (110), 37.0º (103), 37.8º (004), 38.6º (112), 48.0º (200), 53.9º (105), 55.1º (211), 62.6º (204) and 68.8º (116). The crystallite particle size of TiO_2 nanoparticles were found in the range of ~ 21 nm. The pattern recorded was in good agreement with Joint Committee on Powder Diffraction Standard (JCPDS) card number: 89-4921. The particle crystallite size was calculated using the Scherrer's formula equation (eqn. 1):

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (1)$$

where, D is the crystallite size, β = full width at half maximum (FWHM), k is the Scherrer's constant (0.94), λ is the wavelength (Cu*K*α radiation, 1.54 Å), θ is the diffraction point (Bragg's angle).

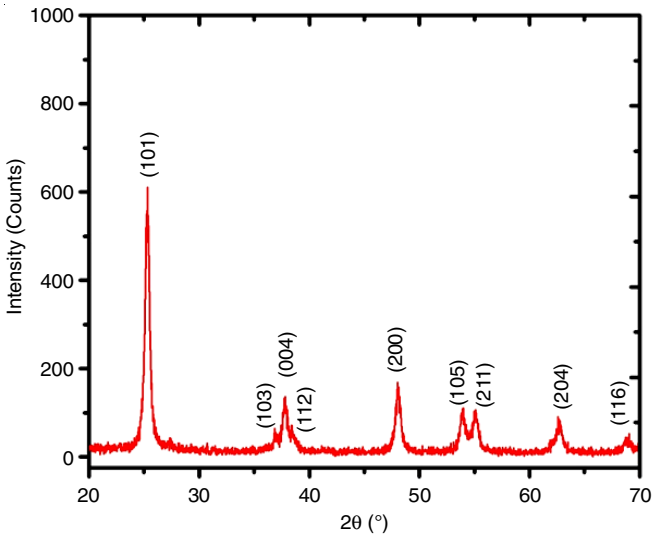


Fig. 1. XRD pattern obtained for the TiO_2 NPs synthesized from aqueous extract of *Ficus benghalensis* leaves

FTIR analysis: The FTIR spectrum was recorded for as-synthesized TiO_2 nanoparticles, which indexes the band range at 3371 cm^{-1} ascribing to the O-H stretching vibration (free water molecules), the band at 1637 cm^{-1} was attributed to the O-H bending vibration (chemically adsorbed water) (Fig. 2). The characteristic peak at 496 cm^{-1} affirms the Ti-O bond indicating that the as-synthesized TiO_2 nanoparticles have greater interaction towards the molecular reaction [22-24].

SEM and EDAX analysis: The green/biogenic synthesized TiO_2 nanoparticles were exposed to SEM and EDAX instruments to study the surface morphology, size/shape and elemental composition to ascertain the atomic percentage, respectively. The SEM image obtained confirmed that the crystallite particles were spherical in shape. The spherical TiO_2 nanoparticles with less agglomeration were observed with particle size of ~ 30 nm to ~ 50 nm. The as-synthesized TiO_2 nanoparticles with captured SEM image having spherical morphology are depicted in Fig. 3a-b. The EDAX spectrum of TiO_2 nanoparticles were recorded to ascertain the elemental

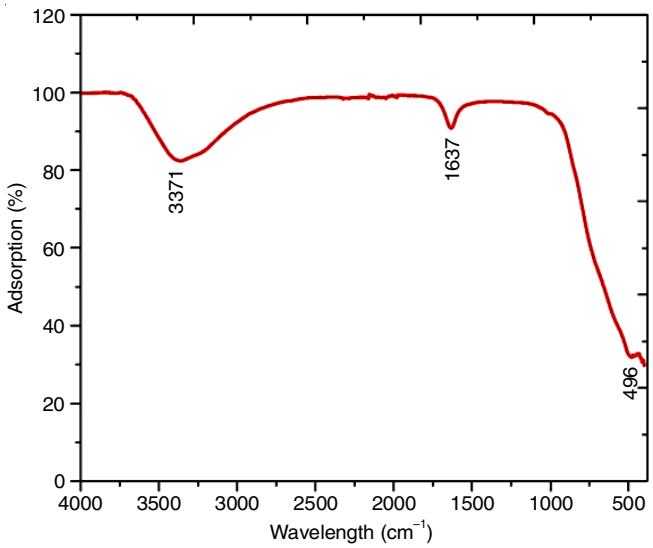
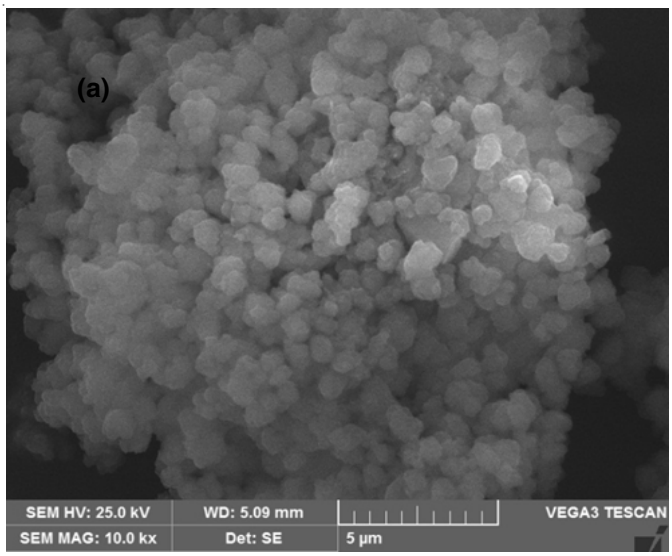
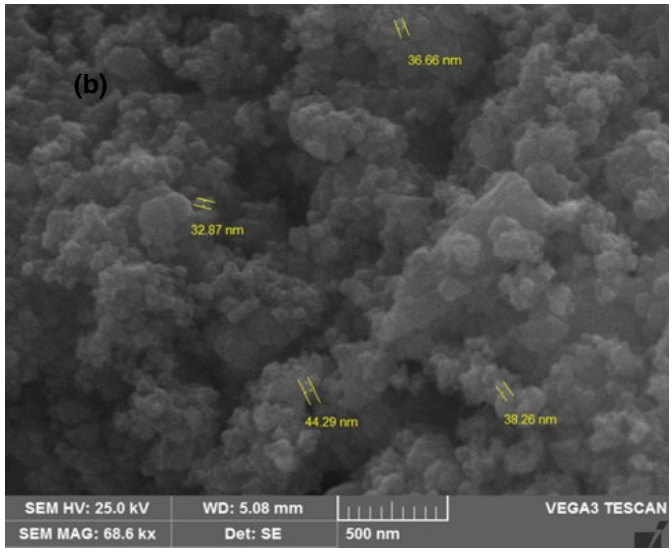


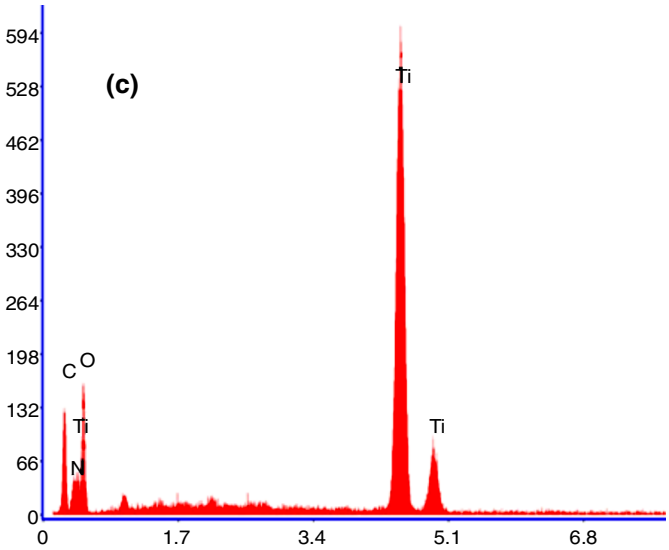
Fig. 2. FTIR profile obtained for the TiO_2 NPs synthesized from aqueous extract of *Ficus benghalensis* leaves

composition with atomic weight percentage (Fig. 3c-d). The spectrum affirms the purity of the as-synthesized nanomaterial also evidences the presence of Ti and O elements in the composition. The EDAX elemental composition detailed that Ti with 35.3%, O with 41.8% and C with 21.4%; indicating the greater percentage of oxygen with Ti and small amount of carbon is an additional for green synthesis which predominantly affirms that green synthesized nanoparticles are covered with capping/stabilizing agents to avoid any further agglomeration when exposed to normal atmosphere [25].

Sensor device fabrication: The schematic illustration of sensor device fabrication is depicted in Fig. 4a and the final view of sensing device with 2 cm × 2 cm as can be seen in Fig. 4b. The n-type Si wafer (SSP) of 2-inch (dia) having resistivity of 0.01-0.02 Ωcm (low) was utilized for the gas sensor fabrication process as initial step. The Si wafer was initially cleaned using RCA (Radio Corporation of America) process which generally follows substrate cleaning ultrasonically with deionized water followed by ethanol wash for 5 min and then







(d)

Element	Weight (%)	Atomic (%)
C K	9.59	21.43
N K	0.73	1.38
O K	33.05	41.85
TiK	61.63	35.34

Fig. 3. Data obtained from SEM-EDAX studies of green synthesized TiO_2 NPs: SEM images at different magnifications: (a) and (b); EDAX spectrum of as-synthesized TiO_2 NPs (c) and elemental composition recorded as presented in the table (d)

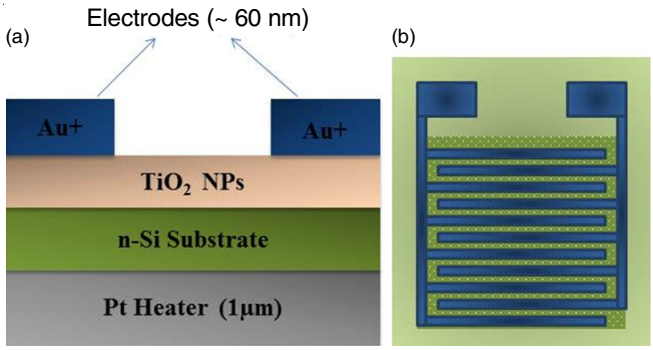


Fig. 4. (a) Fabrication process flow of thin film gas sensor, (b) Overview of sensing device structure

isopropyl alcohol for 5 min to remove any sort of organic contaminations. The cleansed Si substrate was dried at 90 ºC on hot plate to remove water vapours or droplets present after the substrate wash [26].

TiO_2 nanoparticles as-synthesized was spun using spin coater with 2-stage ramp of various rotational speed of 500 rpm for 15 s and 1500 rpm for 30 s and further the substrate was annealed at 120 ºC for 45 min. The thin film layer (~ 100 nm) of TiO_2 nanoparticles was confirmed usimg profilometer studies. The as-incorporated TiO_2 nanoparticles in a solution form was prepared prior to the spin-coat by adding 5 mg of as-synthesized TiO_2 nanoparticles in 5 mL of ethanol (1:1 ratio), which is orthogonal solvent. The contact electrodes Au (~ 60 nm thickness) were deposited (RF magnetron sputtering) using physical mask at 10^{-6} mBar [27]. Platinum resistor for heater was deposited onto the surface (back) of the film (as-deposited) over Si substrate with sputtering (RF magnetron). The side of Pt (1 µm thickness) deposition was used heating coil which plays vital role in sensing mechanism. The sensing device with 2 cm × 2 cm size was finally ready to be tested with analyte (Fig. 4b) and the detection of methanol was affirmed by I-V measurements performed on the as-fabricated thin film gas sensor.

Sensing device characterization: In this work, the sensor is designed over n-type Si substrate with Pt base heating coil and TiO_2 nanoparticles as active layer for the detection of methanol and the sensitivity of the sensor exposed to the measurements purely depend upon resistivity values with varying temperatures from 50-200 ºC for different concentration level of methanol (250, 500 and 1000 ppm) respectively (Fig. 5a-b). The sensor showed excellent sensing characteristics at working temperature of 100 ºC as compared to that of 50, 150 and 200 ºC when exposed to various concentrations as depicted. The sensitivity (average) per ppm (sensitivity/ppm) of sensor designed was found to be excellent. The resistance rapidly increased when methanol was introduced at different concentrations at different temperatures whereas there was rapid decrease when in the absence of methanol indicating the pure sign of detection by varying the electrical characteristics in terms of electrical conducitivity or resistance. The process was repeated for more than 5 times to confirm the reproducibility of sensor device and results affirmed the same behaviour as earlier.

Methanol sensing mechanism: The gas sensing behaviour of the as-fabricated thin film device can be detailed in two different junctures. Firstly, the oxygen adsorption over the sensing device is considered and secondly, the reaction between adsorbed oxygen and the testing analyte over the sensing thin film is considered. The adsorbed oxygen molecules in ambient air gets trapped by electrons from the conduction band of sensing film active media (oxide surface), which further cause reduction at the surface in electron concentration. The methanol molecules are generally regarded as electron rich reducing agent which leads to the large electron transfer. The TiO_2 thin film interact upon exposure to methanol donating electron e^- to the device interface leading to the reduction of barrier height and change in the electrical conductivity [28-30]. In present work, the sensor behaviour is dependent on temperature, when the analyte is exposed at operating temperature the change in electrical conductivity is maximum beyond the operating temperature change in electrical conductivity is minimum. The response may be attributed to the interaction between the adsorption and desorption of chemi-sorbed, which confirmed the temperature dependent behaviour of the designed sensing device.

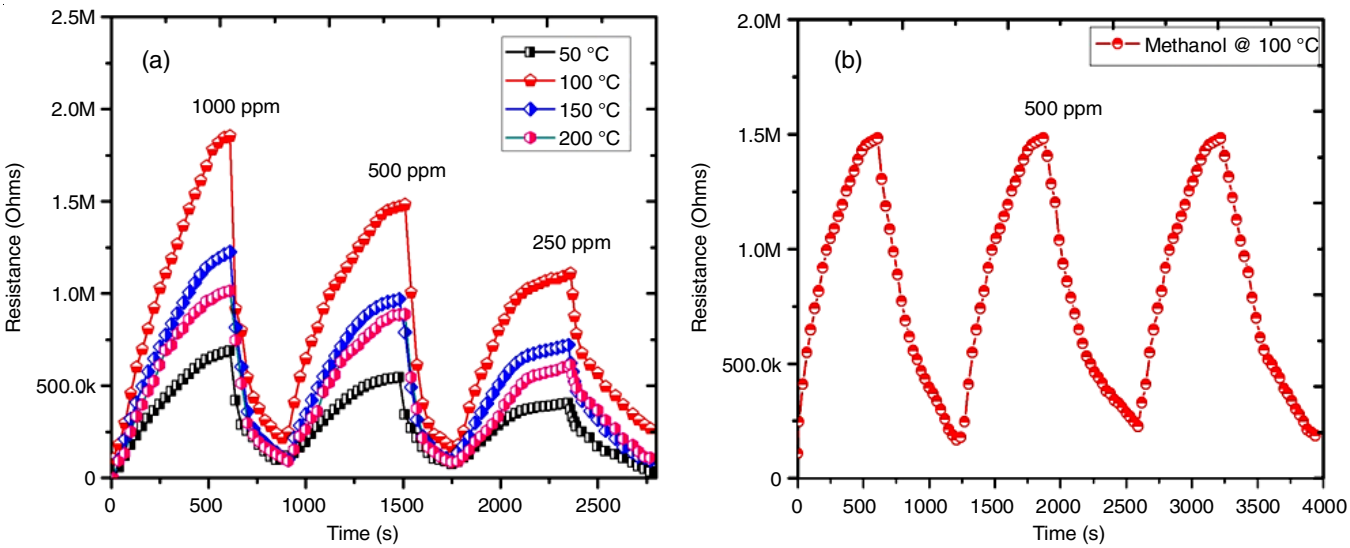


Fig. 5. Gas-sensing characteristics: (a) transient resistance *vs*. time; (b) transient response of the sensor for 500 ppm at 100 °C

Conclusion

The green TiO_2 nanoparticles based thin film sensor for methanol detection has been designed with much economical ways creating the space for new generation of sensors using green nanomaterials promising much better sensitivity and selectivity. The present focuses on green route synthesized TiO_2 describing their unique properties, which were portrayed using various analytical instruments confirming the material characteristics in nanometer range as confirmed by XRD, FTIR, SEM and EDAX. Furthermore, the material was utilized in the detection of methanol by fabricating thin film sensing device to study the change in resistance or electrical conductivity under various temperatures as aforementioned. The sensing device demonstrated that the methanol detection at 100 ºC showed a great response affirming the lowest working temperature of sensor evidencing the green TiO_2 nanoparticles with greater sensing capability. The reproducibility of the device was potrayed with same sensing behaviour for multiple tests carried out exploring the derth for wide range of applications in the field of electronics.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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