Green synthesis of vanadium oxide nanoparticles for thin film based sensor application

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Abstract: A high yield of single phase orthorhombic vanadium oxide (V₂O₅) nanoparticles with solution combustion method is obtained in a very quick succession at 500 °C, by the utilization of Butea monosperma seed extract, to study its suitability towards pressure sensors. The Structural, Transmission spectral, Morphological, Compositional and the Absorption spectral analysis of the deposited vanadium oxide nanoparticle samples are examined using X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM), High resolution transmission electron microscope (HRTEM), Energy dispersive X-Ray analysis (EDX) and Ultraviolet–visible spectroscopy (UV) respectively. The results from the structural analysis denote the nanoparticles with the crystallite size of 4.76 Å, dislocation density of 441.35*10¹⁰/m² along with the micro strain of 76.0366*10⁻³. Infrared transmission spectral images clearly display three strong peaks at 1633.76 cm⁻¹, 1070.80 cm⁻¹ and 537.25 cm⁻¹, stating the presence of a strong and stable vanadyl bonding structure. Images from its morphological analysis depict the nanoparticles are homogeneously porous without any cracks on its surface. The composition of the nanoparticles clearly displays the presence of vanadium and oxygen atoms in a strong bonding structure. Absorption spectral results showed that the obtained samples after synthesis are in nano size with narrow size distribution. The results obtained from the experimental analysis indicate a stable performance, good linearity and stability, indicating its suitability for pressure sensing application.

Key words: Green synthesis; Nanoparticles; V₂O₅; Thin films; Strain gauges.

1. Introduction

In the current trends, pressure is one of those physical quantities which often need to be quantified for many engineering applications such as aerospace industries, bridges in rail monitoring, underground cavities, torque sensors etc. [1]. It is usually defined as the amount of force acting on a surface, per unit area of the substrate or an object [2]. For decades the pressure sensors were usually developed using a strain sensing material attached onto a diaphragm surface with suitable adhesives, but due to their lack of reliability and its detachment from the surface over time, thin films are considered as a remarkable development in the field of strain gauge technology, offering a better alternative [3]. This can be justified from its special characteristics that include low hysteresis loss, good linearity and stability for a longer duration [4]. They also have the ability to maintain the stoichiometry of the target composition and relative simplicity of thickness control, with considerable cost reduction [5, 15].

Vanadium oxide is a promising material and has gained momentum in the field of modern technical and industrial applications because of its ease of synthesis, low cost ingredients with high specific capacity. The material also offers a good safety related properties, high energy density and abundant availability of resources at low price [6]. Out of its many variants amongst the oxide family, the vanadium in its pentoxide form has gained much attention for more than a decade because of its stability and good electrochemical characteristics [7]. They show good metal to semiconductor transition and imply an
abrupt change in optical and electrical properties, because of which the material is being utilized for thermal sensing, switching, smart window, architecture, nanomedicine and automotive applications [8].

The nanoparticles find innumerable benefits in day to day life and they are considered as a special material with its miniature form, exclusive physio-chemical characteristics and electrical properties. They also possess desirable shape, size, dispersion and distribution for thin film based applications [9]. There are various techniques for synthesizing the vanadium oxides that include hydrothermal, sol-gel, spray drying, combustion, microwave irradiation and nanostructural assembling. However in this study, the combustion method is preferred compared to its counterparts, because of its less complex procedure and the ease at which the synthesis can be carried out.

The Butea monosperma plant and its seeds being utilized in the current study for green synthesis are depicted in the figure 1. It is normally found in the tropical and subtropical parts of the Indian subcontinent and is known as the flame of the forest or forest fire [10]. In West bengal this plant has lent its name to the town of Palashi. The development of the pressure sensor based on thin films requires the need of a certain type of material which exhibits long term stability, good sensitivity, linearity and a strong resistance against the atmospheric reactions that acts upon it [11, 16]. The material commonly being utilized in the thin film strain gauges include alloys, cermets, metals, polymers and semiconductors [12, 17]. The current research involving an inorganic compound nanomaterial as the strain gauge is a new adventure in meeting the latest trends. From the extensive literature survey, it was noticed that the exploration of the sensor application based on the \( \text{V}_2\text{O}_5 \) nanoparticles are limited [13], this work based on the development of pressure sensors offer a great deal of opportunity in exploring its potential.

Figure 1. (a) Butea Monosperma (BMS) plant. (b) Its seeds.
2. Experimentation

2.1 Green synthesis of $\text{V}_2\text{O}_5$ nanoparticles using butea monosperma seed extract

The synthesis of vanadium oxide nanoparticles are carried out using combustion, as it offers a simple operating procedure with an excellent yield of product in a very quick succession [14]. The materials required for the synthesis are purchased from Vasa scientific company and the Butea monosperma seeds are collected from the Bannerughatta forest, Bengaluru. The seeds are crushed with a mixer grinder to obtain its fine powder form and then transferred onto a beaker containing distilled water. A mixture of 15 g ammonium metavanadate ($\text{NH}_4\text{VO}_3$) is dissolved inside the beaker containing 90 ml of monosperma seed extract and sonicated for about half an hour. Then the solution containing the mixture is transferred onto the crucibles for combustion in the muffle furnace for 8 hours at 500 °C to obtain the foam like extract. These samples are crushed with a mortar pestle to bring it down into a small particulate structure, which is subjected for calcinations at 520 °C to obtain the fine vanadium oxide nanoparticles.

3. Results and Discussions

The obtained vanadium oxide nanoparticle samples are subjected to various characterization techniques, to check its suitability for pressure sensing application, which are being discussed in the following section.

3.1 Structural Analysis

The results from the structural analysis of the synthesized nanoparticles obtained from the XRD are displayed in the figure 2. The image indicates strong diffraction peaks at $(0\ 2\ 0)$ $(0\ 0\ 1)$ $(0\ 1\ 1)$ $(0\ 4\ 0)$ $(1\ 0\ 1)$ $(1\ 3\ 0)$ $(0\ 1\ 2)$ $(0\ 6\ 0)$ $(2\ 0\ 0)$ $(2\ 4\ 0)$ $(2\ 3\ 2)$ $(1\ 3\ 3)$ $(2\ 6\ 1)$ and so on, representing the orthorhombic crystalline phase of vanadium oxide nanoparticles. The crystallite size ($D$) of 4.76 Å, dislocation density ($\delta$) of $441.35 \times 10^{16}/\text{m}^2$ and the micro strain ($\varepsilon$) of $76.0366 \times 10^{-3}$ determined from the data, in comparison to that of the existing protocols, presented an optimized process parameters indicating its suitability towards sensor development. They are also tabulated in the Table 1. The observed strong peaks at two location from the results at $(0\ 0\ 1)$ and $(1\ 1\ 0)$ indicate the absence of any organic impurities [18, 19]. The other small narrow and intense peaks denote the synthesized nanoparticles are highly crystalline, which contributes to the increased sensitivity of the pressure sensor.

| Sample                  | Crystallite Size ($D$) | Dislocation Density ($\delta$) | Micro Strain ($\varepsilon$) |
|------------------------|------------------------|-------------------------------|-----------------------------|
| $\text{V}_2\text{O}_5$ (BMS seeds) | 4.76 Å             | $441.35 \times 10^{16}/\text{m}^2$ | $76.0366 \times 10^{-3}$   |
| $\text{V}_2\text{O}_5$ (Moringa leaf)  | 3.18 Å             | $986.21 \times 10^{16}/\text{m}^2$ | $113.69 \times 10^{-3}$   |
| $\text{V}_2\text{O}_5$ (Sutera cordata) | 2.27 Å             | $1343.72 \times 10^{16}/\text{m}^2$ | $159.29 \times 10^{-3}$   |
3.2 Transmission spectral Analysis

The FTIR spectrum is depicted in the Figure 3. It is used to obtain the infrared transmission spectrum, chemical bonds and the functional group of the vanadium oxide nanoparticles, they were analyzed in the range of 400-4000 cm⁻¹ wave number (Bruker instrument is used in this analysis). The peaks observed from the results indicate three characteristic vibration modes. The one at 1070.80 denotes V=O vanadyl stretching mode, 537.25 denotes V-O-V symmetric stretching, 1633.76 denotes V-O-V asymmetric stretching around the bonding structure [20]. The results also denote the orthorhombic crystalline structure of the vanadium oxide nanoparticles, which contributes to the better performance of the film if being utilized for the strain gauge application.

![FTIR spectrum of synthesized V₂O₅ nanoparticles](image1)

**Figure 3.** FTIR spectra of the synthesized V₂O₅ nanoparticles.

![XRD spectrum of synthesized V₂O₅ nanoparticles](image2)

**Figure 2.** XRD spectrum of the synthesized V₂O₅ nanoparticles.
3.3 Morphological studies

The SEM images are depicted in the Figure 4. They convey the rod like morphological structure of the calcinated samples with a strong vanadium oxide bonds in the size range between 0.2-10 µm, when operated at 10 kV. The structures of the calcinated nanoparticles are homogenously porous without any crack on its surface. The smallest diameter of which was observed to be of 10 nm.

![Figure 4. SEM images of the synthesized V_2O_5 nanoparticles.](image)

The HRTEM images of nano V_2O_5 is presented in the Figure 5. The actual size of the particle, their grain growth and the distribution of the crystallites can be determined out of it. The results obtained indicate a sheet like structure of the given vanadium oxide samples. The rod shaped image in the figure denotes the presence of carbon from the precursor and the black spots in it indicates the vanadium oxide bonding structure [21]. The crystalline nature of the samples can be recognized from the given images and the presence of lattice planes in the size ranges between 2-5 nm is clearly visible from it. The distance between the two planes, which are obtained to be of 0.563 nm, show a clear indication of high crystallite size and the lattice constant of the vanadium oxide nanoparticles, which is necessary for pressure sensing application [22]. There is an observed uniformity of the crystallite structure in the size range of 5-10 nm.
3.4 Compositional analysis

EDX operated at 10 kV is used for the compositional analysis of the given vanadium oxide nanoparticles. The results are displayed in the Figure 6. It confirms the presence of vanadium oxide along with some traces of aluminum and carbon which is from the stub/sample holder, which is not to be quantified. From the results obtained, it was noted that the atomic mass percentage of vanadium and oxygen are 56.01 and 43.98, the weight percentage of the same are noted to be of 50.94 and 15.99 respectively. The results are tabulated in the Table 2.

Figure 5. HRTEM images of the synthesized V₂O₅ nanoparticles.

Figure 6. EDX spectrum of the synthesized V₂O₅ nanoparticles.
Table 2. Atomic mass and Atomic Weight Percentages of the synthesized V$_2$O$_5$ nanoparticles.

| Element       | Atomic Mass % | Atomic Weight % |
|---------------|---------------|-----------------|
| Vanadium (V$_2$) | 56.01         | 50.94           |
| Oxide (O$_5$)  | 43.98         | 15.99           |

3.5 Absorption spectral analysis

The absorption spectrum of the V$_2$O$_5$ nanoparticles is presented in the Figure 7. It is conducted to find the optical band gap energy level, which is calculated by the relation $1242/\lambda$ and their band gap energy was found that to be of 2.5 eV. The spectral width of the absorption spectrum was attributable to the size distribution of the particles with diverse sizes. The absorbance of the samples decreases slightly with increase in annealing. The sharp peaks show that the particles are in nano size with narrow size distribution. The absorption peaks of V$_2$O$_5$ shows a blue shift in comparison with that of the bulk V$_2$O$_5$, which is attributed to the quantum confinement effect happened during the electronic transition from the occupied 2p bands of oxygen to the unoccupied 3d bands of V$_2$O$_5$. A red shift is observed in the characteristic absorption peak due to the decrease in the band gap of the samples [23].

![Figure 7. UV spectroscopic data of the synthesized V$_2$O$_5$ nanoparticles.](image)

4. Conclusions

Hence by this experimental investigation, it can be concluded that the method of synthesis used in this correspondence gives a better yield of the vanadium oxide samples, whose characterization results clearly indicate a strong vanadium oxide nanoparticles without any organic impurities. The calcinations of the synthesized nanoparticles resulted in good crystalline structure. The adequate crystallite size of 4.76 Å observed from the structural analysis, provides good response to the smallest of change in pressure applied on the surface of the film. The reduced dislocation density 441.35*10$^{16}$/m$^2$ along with the micro strain of 76.0366*10$^{-3}$, determined from the diffraction results helps in the increased sensitivity of the pressure sensors. The orthorhombic crystalline structure of the nanoparticles, observed from the infrared
transmission spectrum, with the presence of three characteristic stretching modes, contributes to the better performance of the strain gauges. The rod like morphology with the absence of any cracks on its surface, serves to improve the durability of the sensors. Hence from the results obtained, it can be concluded that the V$_2$O$_5$ nanomaterial based thin films offer a better alternative for pressure sensor development in overcoming some of the drawbacks associated with the existing pressure sensors.

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References

[1] Kalpana H M and Prasad V S 2014 Development of the invar36 thin film strain gauge sensor for strain measurement Meas. Sci. Technol. 25 065102
[2] Yuan Y Li M and Xu J 2011 A pressure sensor study and research IEEE 2nd Int. Conf. on Computing, Control and Industrial Engineering, Wuhan, China 11 255-58
[3] Mihara Y and Someya T 2002 A study on the development of a thin-film pressure sensor IEEE Sensors 2 954-59
[4] Kalpana H M, Prasad V S and Nayak M M 2013 Influence of annealing and thickness on the electrical properties of invar36 thin film for strain gauge applications IJTFST 2 155
[5] Witt G R 1974 Thin Solid Films 22 133-56
[6] Liang X, Gao G, Liu Y, Zhang T and Wu G 2017 Synthesis and characterization of Fe-doped vanadium oxide nanorods and their electrochemical performance J. Alloys Compd. 715 374-83
[7] Liu X, Zeng J, Yang H, Zhou K and Pan D 2018 V$_2$O$_5$-based nanomaterials: synthesis and their applications RSC Adv. 8 4014-31
[8] Zeng H, Liu D, Zhang Y, See K A, Jun YS, Wu G, Gerbec J A, Ji X and Stucky G D 2015 Nanostructured Mn-doped V2O5 cathode material fabricated from layered vanadium jarosite Chem. Mater. 27 7331-36
[9] Raghavendra M, Yatish K V and Lalithamba H S 2017 Plant-mediated green synthesis of ZnO nanoparticles using Garcinia gummi-gutta seed extract: Photoluminescence, screening of their catalytic activity in antioxidant, formylation and biodiesel production Eur. Phys. J. Plus 132 1-12
[10] Jhade D, Ahirwar D, Sharma N K, Jain R and Gupta S 2009 Butea monosperma (Lam.) taubert: a review J. Pharm. Res. 2 1181-83.
[11] Rajanna K, Muralidhar G K, Nair K G M, Panchapagesan T, Nayak M M, and Mohan S 2014 Effect of strain and temperature on the behavior of oxygen ion implanted manganese films J. Appl. Phys. 76 3573-78
[12] Almassri A M, Wan Hasan W Z, Ahmad S A, Ishak A J, Ghazali A M, Talib D N and Wada C 2015. Pressure sensor: state of the art, design, and application for robotic hand J. Sens.
[13] Ramasami A K, Reddy MV, Nithyadharseni P, Chowdari B V R and Balakrishna G R 2017 Gel-combustion synthesized vanadium pentoxide nanowire clusters for rechargeable lithium batteries J. Alloys Compd. 695 850-58
[14] Jagadeesh A, Rattan T M, Muralikrishna M and Venkataramaniah K 2014. Instant one step synthesis of crystalline nano V2O5 by solution combustion method showing enhanced negative temperature coefficient of resistance Mat. Lett. 121 133-36
[15] Kalpana H M, Prasad V S and Satish T N 2019. Effect of Annealing on Hardness and Elastic Modulus of Invar36 Thin Films Deposited by Direct Current Sputtering for Strain Gauge
Applications IJTFST 8 4

[16] Rakshit A, Biswas D and Chakraborty S 2018 Deposition and characterization of vanadium oxide based thin films for MOS device applications In AIP Conf. Proceed. 1942 120024

[17] Jin Y, Basantani H A, Ozcelik A, Jackson T N and Horn M W 2013 High-resistivity and high-TCR vanadium oxide thin films for infrared imaging prepared by bias target ion-beam deposition. In Infrared Technology and Applications 8704 87043C

[18] Chan Y L, Pung S Y and Sreekantan S 2014 Synthesis of V2O5 nanoflakes on PET fiber as visible-light-driven photocatalysts for degradation of RhB dye J. Catal.

[19] Mihara Y and Someya T 2002 A study on the development of a thin-film pressure sensor IEEE Sensors 2 954-59

[20] Zhu K, Meng Y, Qiu H, Gao Y, Wang C, Du F, Wei Y and Chen G 2015 Facile synthesis of V2O5 nanoparticles as a capable cathode for high energy lithium-ion batteries J. Alloys Compd. 650 370-73.

[21] Nalini S, Selvakumar B and Periasamy P J I J E M S 2017 Simple synthesis and characterization of V2O5 nanoparticles by microwave assisted wet chemical method Int. J. Eng. Manuf. Sci 7 411-17

[22] Farahmandjou M and Abaeiyan N 2017 Chemical synthesis of vanadium oxide (V2O5) nanoparticles prepared by sodium metavanadate J. Nanomedicine Res. 5 00103

[23] Derkaoui I, Khenfouch M, Elmokri I, Mothudi B M, Dhlamini M S, Moloi S J, Zorkani I, Jorio A and Maaza M 2017 Structural and optical properties of hydrothermally synthesized vanadium oxides nanobelts IOP Conf. Ser.: Mater. Sci. Eng. 186 012007