Properties and Biomedical Applications of Hydrothermal method Synthesized of Vanadium Oxide nanoparticles

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Abstract:
Vanadium oxide thin films were successfully prepared hydrothermally and deposited on a substrate using the drop casting method. Analytical techniques such as XRD, AFM, (SEM) analyses, Ultraviolet-Visible (UV-Vis), PL, and FTIR measurements were used to confirm the characterization of the prepared vanadium oxide NPs. The XRD measurements show that the VO2 thin film was polycrystalline, with a (monoclinic) phase and crystallite size calculated using Scherrer's equation, as well as dislocation density and microstrain. The optical properties show that the energy gap (4.49) eV, and depending on PL, a single sharp emission peak was found at location 350 nm (3.54 eV). The Antibacterial activity of the vanadium oxide nanoparticles were investigated, with inhibition zone Escherichia coli (17) mm, Staphylococcus aureus 20 mm, Bacillus subtilis 18 mm, and Klebsiella pneumonia 19 mm and Candida isolates 15 mm. The study confirms that the prepared VO2 samples can be used as an antibacterial agent. The results suggest that proper tuning can make them a good antimicrobial agent.

Keywords: Vanadium dioxide, thin film, Hydrothermal, Antibacterial Activity

1-Introduction
Vanadium oxide exists in a number of different stoichiometries. The transition from semiconductor to metal (also known as metal-insulator (MIT)) occurs at around 68 oC for VO2, and is followed by a first-order structural phase transition from a monoclinic to a tetragonal structure [5]. This phase transition is associated with abrupt changes in the physical properties of VO2, particularly its optical and electrical properties. Thermal sensors, electrical switches, smart windows, optical limiting, modulators, IR cooled bolometers, Mott-field effect transistors, switchable tunnel barriers, and thermal energy management all benefit from such a diverse range of nanostructured VO2 materials [6-10]. Vanadium produces a variety of oxygen-containing compounds, including VO, V2O5, V2O3, V4O9, and VO2. Vanadium oxide thin films can be created using a variety of techniques, including pulsed laser deposition (PLD), electron beam evaporation, and magnetron sputtering, sol-gel process, spray pyrolysis (SP) and hydrothermal synthesis. The preparation method and deposition parameters influence on the properties of the prepared films [5, 11, and 12]. In this paper, we report the
preparation of VO₂ NPs by hydrothermal method and study the effect of vanadium oxide nanoparticles against bacterial isolates.

2-Experimental part
The material NPs were synthesized using a simple chemical method (SCM), with a mixture of 3g powder of material added to 100 ml of distilled water, and the solution placed on a magnetic stirrer for 15 minutes at 80 °C before cooling to room temperature. To deposit on a glass substrate, the Drop casting technique was used. The solution was taken with a pipette and dropped onto the glass surface substrate about 4 drops, then the films were dried up using an 80°C heater. Figure (1) shows the preparation and deposition method.

![Figure (1): schematic diagram of hydrothermal method and drop casting.](image)

A well-diffusion method was used to test the antibacterial and antifungal activity of vanadium oxide nanoparticles against pathogenic bacteria. Plates were formed by spreading approximately 10⁵ cfu/ml culture broth of each indicator bacterial isolate on the surface of nutrient agar. Before aseptically dispensing the 50l of agar plates, the agar plates were left for about 15 minutes.

3-Result and dissection
X-ray diffraction analysis
To study the structure of the prepared films, XRD patterns were recorded using SHIMADZU™ XRD-6000 X-ray, power diffraction system using CuKa (k = 0.15406 nm) radiation. Figure (2) shows the diffraction pattern of the Vanadium oxide thin films deposited on glass substrates using drop casting. Three diffraction peaks could be seen which corresponded to (010), (002) and (020) orientation planes, this agree with card number (00-032-1399). Thin film was polycrystalline, monoclinic phase this agreement [13]. The crystallite size was estimated of the deposited films by using the Scherrer’s formula. The dislocation density (δ) was calculated using Williamson and Smallman’s formula and Microstrain [14] as in Table (1):

\[ C.S = \frac{0.94\lambda}{FWHM \cos \theta} \]  
\[ \delta = \frac{1}{(G.S)^2} \]  
\[ Strain = \frac{FWHM \cos \theta}{4} \]

![Graph](image)
Table 1 Summary of XRD parameters, crystallite size dislocation density and Microstrain

| 2 Theta (deg) | FWHM (deg) | hkl planes | G.S nm | δ x10^14 lines.m^-2 | Microstrain x 10^-4 lines^2.m^-4 |
|---------------|------------|------------|--------|---------------------|-------------------------------|
| 12.33         | 0.437      | (010)      | 18.28023 | 29.92518            | 18.95491                      |
| 24.83         | 0.4        | (020)      | 20.33489 | 24.18335            | 17.03968                      |
| 28.03         | 0.28       | (002)      | 29.24301 | 11.69381            | 11.84899                      |

Morphology and Topography Surface Vanadium Oxide Thin Films

The AFM instrument is used to examine the surface morphology and roughness of the films. Figure (3a) shows a scan area of 49.5x50 m² for a thin VO₂ film image. The image shows that the dark areas represented areas with a positive direction of zero or near zero height value, whereas the bright areas represented higher areas, such as the top of the bulging grains. The film's surface was even and continuous. The grain size of the film was 1.78 m. The SEM image of the film deposited on the substrate at room temperature is shown in Fig. (3b). The film surface is made up of grain distributions with particle sizes estimated to be (4.46, 2.70, 5.44.) m. Spherical-like grains were observed, indicating that the grains were in the VO₂ (M) phase [15].

Optical properties of vanadium oxide thin film

The optical transmittance spectra (in the wavelength range of 200–900 nm) of drop casting vanadium oxide thin films at room temperature are shown in Figure (4). The deposited vanadium oxide film had a high transmittance that increased with increasing wavelength. The region with the highest transmittance is record (92–86) percent in the range (360-570) nm. Low surface roughness detected in AFM analysis may result in low light-scattering loss, resulting in high optical transmittance [16].
The optical band gap of the films was calculated using the equation \((\alpha h v)^2 = A(h - E_g)\), where \((A)\) is a constant, \((v)\) is the frequency of the radiation, \(E_g\) is the band gap, and \(\alpha\) is the absorption coefficient. The extrapolation between \((\alpha h v)^2\) and energy \((h v)\) of the graph plotted is shown in Fig. (5), to estimate optical band gap value is 4.0 eV, indicating that the quantum size effect causes the band gap to increase.

![Graph showing optical transmittance spectra](image1)

**Figure (4). Optical transmittance spectra of the vanadium oxide film at room temperature.**

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![Graph showing relationship (alpha hv)^2 vs photon energy](image2)

**Figure 5. The relationship \((\alpha h v)^2\) as a function of \((h v)\) for vanadium oxide.**

Figure 6, the PL spectrum of vanadium oxide is recorded from 200 to 450 nm in the scale of wavelength at room temperature. Single sharp emission peak at location 350 nm (3.54 eV). The observed PL blue shift peak showed disagreement with optical band gap that estimated from the absorption, this difference is attributed to the effect of the quantitative size.
The infrared spectrum of vanadium oxide is shown in Figure (7); the observed infrared spectrum has stretching vibrational modes of \( \text{V}--\text{O} \) groups at 707 cm\(^{-1}\). This agreement with Ref [17] is achieved by stretching vibrational modes of the vandal group \( \text{V}=\text{O} \) at 983 cm\(^{-1}\). The peak between 3200 and 3600 cm\(^{-1}\), depending on the strength of the hydrogen bonding, is expected to belong to \( \text{O}--\text{H} \) vibrations, whereas the band at 1099 cm\(^{-1}\) is assigned to the oxidation state transition from V\( ^{5+} \) to V\( ^{4+} \). Structured paraphrase [18].

The effect of vanadium oxide nanoparticles in combination with various antibiotics and antifungal were investigated against pathogenic bacteria (Escherichia coli, Staphylococcus aureus, Bacillus subtilis, and Klebsiella pneumonia and Candida isolates) using the method of disk diffusion (method of agar well) as shown in Fig (8). The results showed clearly those NPs of vanadium oxide were effective against antibacterial and antifungal isolates as shown in Table (1) against isolates, the diameter of the inhibition zones (mm) around the various antibiotic discs with and without vanadium oxide nanoparticles was measured. The results showed that Staphylococcus aureus outperforms the others in terms of bacterial activity. Because of electrostatic attraction, the antibacterial effect of VO\(_2\) NPs is primarily due to attachment to the bacterial cell wall, suggested mechanisms involving the interaction of nanomaterials with biological molecules due to the different charges, resulting in attraction between bacteria and treated surface, leading to oxidization of microbes and finally death. Antibiotic molecules contain several active groups, such as amino groups and hydroxyl, which react with nanoparticles via chelation, resulting in a synergistic effect [19-20].

![PL spectrum](image1)

**Fig. 6: PL for vanadium oxide thin films as a function of wavelength**

![FTIR spectrum](image2)

**Fig. 7: FTIR analysis of vanadium oxide**
Table 2. Antimicrobial and Antifungal effect of vanadium oxide NPs.

| Compound             | Candidiasis (mm) | Escherichia Coli (mm) | Klebsiella Pneumonia (mm) | Staphylococcus Aureus (mm) | Bacillus Subtilis (mm) |
|----------------------|------------------|-----------------------|--------------------------|----------------------------|------------------------|
| Vanadium oxide       | 15               | 17                    | 19                       | 20                         | 18                     |

Conclusions

In this work, the chemically prepared vanadium oxide thin film (a simple, low-cost, and quick method) was clearly demonstrated. XRD analysis revealed that the film has a polycrystalline structure. The prepared film appears transparent, and the energy band gap is found to be (4.49 eV), indicating that the energy gap is increasing due to the quantum size effect. The main application of vanadium oxide nanoparticles was inhibitory influence against some pathogenic bacteria, and it was discovered that the diameter of inhibition zones of VO₂ NPs on Escherichia coli (17 mm), Staphylococcus aureus (20 mm), Bacillus subtilis (18 mm), Klebsiella pneumonia (19 mm), and Candida isolates (15 mm).

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