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Selection of an Optimum Technique for Synthesis of Thermochromic VO_2 for Energy and Environmental Applications

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ABSTRACT

This paper reports the successful synthesis of VO_2 nanoparticles via three different techniques and a comparative study. XRD is done for identification of the synthesized materials. FTIR is done for chemical composition and transmittance in the particular range. UV-VIS spectrophotometer is done for finding energy band gap and for absorbance. For surface morphology, scanning electron microscopy is done. For confirmation of particle size, tunneling electron microscopy is done. For making material commercially viable, comparison between techniques is done. It is observed that hydrothermal method is better as compared to others due to its properties as cheapness and easy to use which make it commercial for smart windows.

KEYWORDS

Hydrothermal method, Low temperature method, Microwave assisted solution based method, VO2, metal-insulator transition, UV-Vis, SEM, TEM, XRD.

Introduction

From past several years, oxides of transition metals such as vanadium with multiple valance states, such as V_6O_{13}, V_2O_5, V_2O_3 and VO_2, have fascinated researchers to explore their properties for wide-ranging applications [1] - [9]. These oxides show enormous potential in electrical [10]–[13], optical[14]–[16], thermal[17]–[19], magnetic[20]–[22] and energy saving applications, [23][24], which makes these Vanadium oxides qualitatively different from other transition metal oxides. It is of primary interest for researchers to synthesize materials with new structures, sizes and shapes, which may have attractive properties. As vanadium has several oxidation states (0 to +5), which exist with even magnetic structures, defined by the general formula V_nO_{2n-1} ($2 \leq n \leq 9$) and V_nO_{2n+1} - they make a homologous series of compounds with structurally and energetically similar crystal structures. Information about homologous series for molybdenum and vanadium oxides was reported for the first time by Magnéli [25]. Among all vanadium oxides, monoclinic Vanadium dioxide (VO_2 (M)) demonstrates a rare phase transition temperature near to room temperature at about 68°C. During this transition, the oxide phase changes from higher temperature metallic phase to a lower temperature semiconductor phase due to unit cell distortions - this is a reversible switch in which variable absorbance in UV region, transmittance in visible region and reflectance in IR region take place. Below the phase transition temperature, it shows a monoclinic structure with P21/c space group which allows infra red light to pass unabsorbed or reflected, which means that for IR it is behaving like conductor, but above the transition temperature, it has a tetragonal structure with $P4_2/mnm$ rutile space group, which, being metallic due to the

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presence of mobile electron cloud, does not allow infrared light to pass through itself and that means it behaves as an insulator/reflector for IR wavelengths of the solar spectrum. If this transition can be controlled and tuned, then it this can become highly useful in many applications, as mentioned above.

More than ten types of VO_2 phases have been studied, some of which are a low temperature tetragonal phase VO_2 (A) (P4/ncc), a high temperature tetragonal phase VO_2 (A) (I4/m), monoclinic VO_2 (B) (C2/m) and a tetragonal rutile-type phase VO_2 (R). Among these vanadium dioxides VO_2 (B/A) are used as precursors for synthesizing VO_2 (M/R) and it is found to be very hard to synthesize VO_2 (M1) in a single step, even though it has been claimed to have been achieved by few researchers in a one-step hydrothermal reaction [26]–[32]. Many routes has been used for synthesis of doped or undoped VO_2 powders – such as a chemical method [33], spray pyrolysis [34], sol gel method [35], hydrothermal method [36]; and for fabrication of thin films – sputtering method [37], [38], chemical vapor deposition [39] and pulsed laser deposition [40].

Doping is an important technique for tuning of the MIT (Metal-Insulator Transition) temperature as well other optical, electrical properties of VO_2. There is an imperative to optimize the ratio of vanadium source and reducing agents for synthesis of pure form of VO_2 by a method which is easy to use and a cost effective method. Herein, we report on the synthesis of VO_2 by an uncommon method by optimizing the ratio of vanadium pent oxide and citric acid monohydrate precursors.

Experimental

Materials: All the reagents used in the experiments were of analytical grade and used without further purification. Vanadium pentoxide (V_2O_5, AR, CDH) and citric acid monohydrate ($C_6H_8O_7.H_2O$, AR, CDH)) were used as a source of vanadium and reducing agent respectively. Deionized water (5.5×10^{-6} S/m) was taken as a solvent. Ethanol and distilled water were used for washing purpose.

Synthesis:

Hydrothermal method

The source of vanadium dioxide, Vanadium pentaoxide (V_2O_5 , 2 mmol) was dissolved in 23mL of deionized water. After stirring for 5 minutes using a magnetic stirrer, 3 mmol of citric acid monohydrate was added into the solution and the stirring prolonged for 15 minutes. The resultant solution was transferred into a Teflon lined of stainless steel autoclave. The sealed autoclave was kept in oven at 220ºC for 2-12 hrs. After the reaction process is complete, the autoclave was slowly cooled to room temperature. The as-prepared powder samples were centrifuged, filtered and washed with ethanol and distilled water to remove unreacted chemical species, and dried in air at 80ºC overnight. The finally obtained product was a dark blue-black powder (Sample 1) used as is for further characterizations.

Low temperature chemical method:

The source of vanadium dioxide, Vanadium pentoxide (V_2O_5, 2 mmol) was dissolved in 23mL of deionized water and 3 mmol of citric acid monohydrate was added into the solution in round bottom flask placed in oil bath at 160ºC. The temperature was maintained using a condensation set up and the entire setup rests on a round bottom flask kept inside an oil bath which is kept on a magnetic stirrer. After stirring for 6 hrs, the as-prepared samples were centrifuged, filtered and washed with ethanol and distilled water. After that, the precipitate was then placed in an oven at 200ºC for 30 minutes to produce a black powder. After cooling to room temperature, the prepared sample was mixed with ethanol and sonicated for 2 min to form a suspension. The suspension was filtered and the resultant precipitate was treated in an oven at 200ºC for 30min. This final product was named as Sample-2 powder was used for further characterization.

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Microwave assisted solution based method

The source of vanadium dioxide, Vanadium pentoxide (V_2O_5, 2 mmol) was dissolved in 23mL of deionized water at 60°C. After stirring for 20-30 minutes using a magnetic stirrer, 3 mmol of citric acid monohydrate was added into the solution and stirring continued for 30 minutes. The solution turned yellow and finally blue, indicating the reduction of V^{5+} to V^{4+}. After stirring, the solution is dried in a microwave oven. Microwave irradiation used was at 200W and the dried agglomerated sample is obtained. Thereafter the sample is dispersed in ethanol, and the mixture is sonicated and filtered. The as-prepared sample was kept in an electric oven under effect of IR radiation. The finally obtained black powder named as Sample-3 was used for further characterization.

Characterization:

The resulting samples prepared by different techniques were characterized by X-ray diffraction (XRD, Rigaku Ultima IV, with CuK_α (λ=0.154nm) radiation) with a diffraction angle between 20 to 80°C. Crystalline size (D) was estimated from Scherrer's equation:

$$D=K\,\lambda/\beta\cos\theta \qquad (1)$$

where K is the Scherrer's shape factor with value 0.9, λ is the Cu Kα X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians and θ is Bragg angle. D is the mean size of ordered (crystalline) domains, which may be smaller or equal to the particle size. The surface morphology of prepared samples was investigated a by Scanning Electron Microscope (SEM) (JEOL). For examining the purity and chemical compositions, these samples were tested by FTIR spectroscopy (Frontier, Perkin Elmer). Optical properties were characterized by UV-VIS spectrophotometer (UV-2401 PC Shimadzu). The optical energy band gap of materials was found using Tauc plot obtained from UV-VIS test using the equation as follows:

$$(\alpha\hbar\omega)^m = A(\hbar\omega - E_g) \qquad (2)$$

Here the value of m depending on the optical transition nature, was ½, 1/3, 2 and 2/3 for indirect allowed, indirect-forbidden, direct allowed and direct forbidden optical transition, respectively[41]. Using the above equation, by linear extrapolation of the tangent at the inflection point of the $(\alpha\hbar\omega)^m$ versus $\hbar\omega$ plot, we can estimate the energy band gap at α=0 axis intercept. The supporting information regarding crystal sizes is obtained from Transmission Electron Microscope (TEM) (TECNAI G-20) operated at an acceleration voltage of 200kV.

Results and Discussion

X-ray Diffraction

For identification of materials**,** it was performed using JCPDS Card and indexing as shown in fig1. Indexing of XRD graph was done by JCPDS Card, by which we can say successful synthesis observed. The XRD of samples shows common peaks at 2θ is 25.5°, 29°, 30.5°, 30.8°, 34° and 45.8°. These peaks denote monoclinic vanadium dioxide according to JCPDS data card with space group C2/m and space lattice a= 9.083, b= 5.76 and c= 4.53 Å, with angle β=91.3°. After calculation using Scherer's equation (1), average size of crystallites is 16 nm, 23 nm and 35 nm for sample 1, sample 2 and sample 3 respectively.

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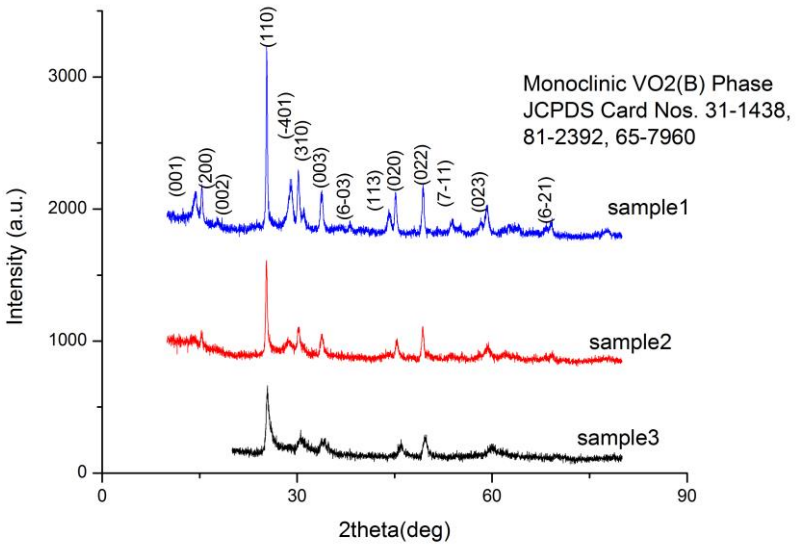

Fig 1: XRD patterns of sample (1), sample (2) and sample (3) prepared by hydrothermal method, low temperature method, and microwave assisted solution based method, respectively.

Scanning electronic microscopy

The images obtained by SEM imaging shows the morphology of VO2 phase particles to be nano-sized and platelike in structure. (Fig. 2).

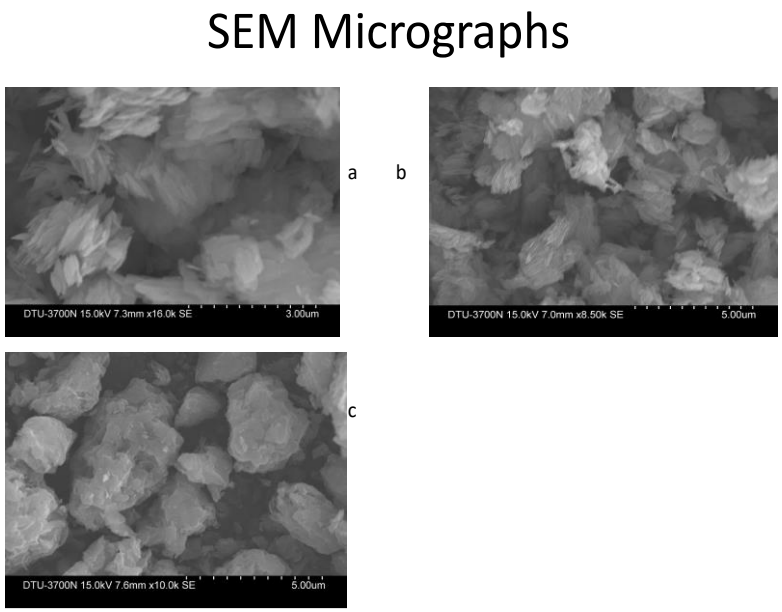

Fig 2: SEM images taken at different scale (a) 3µm, (b) 5 µm and (c) 5 µm of sample 1, 2 and 3 prepared by hydrothermal method, low temperature method and microwave assisted solution based method respectively.

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Infrared spectroscopy

Obtained results show study of structure information by apparition and disappearance of chemical function from vibration modes of liaisons of molecule.

To investigate the chemical bonding between vanadium and oxygen ions and to confirm the phase purity, FTIR spectroscopy was performed. Fig.3 shows the FTIR spectrum of VO2 (B) samples prepared by different techniques. The main vibrational bands observed from the FTIR spectrum are at 551, 786, 1012, 1624, 2339, and 2541cm^{-1} and can be attributed to the various vibrational bands of V−O, O−H, and C−O systems . From the comparison with the spectra of pure KBr, only bands at 551, 936, and 1012 cm^{-1} can be considered as vanadium oxide, which matches well with earlier reports: the initial broad vibrational band at 551 cm^{-1} is assigned to the V−O−V octahedral bending modes, the band at 936 cm^{-1} is attributed to the coupled vibration of V=O and V−O−V and the band at 1012 cm^{-1} can attributed to the stretching of short V−O bonds that are also present in this phase [42]–[46].

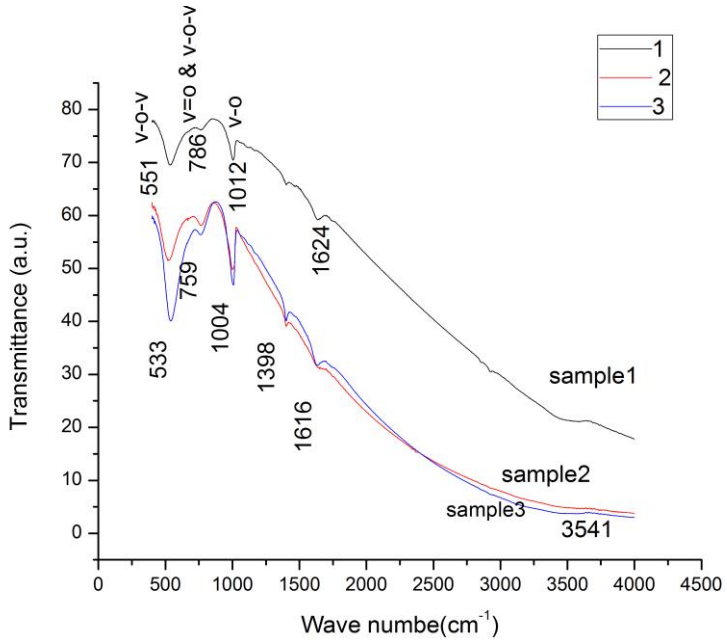

Fig. 3: Transmittance corresponds to wave number of synthesized samples 1, 2 and 3, prepared by hydrothermal, low temperature method and microwave assisted solution based methods, respectively.

UV-VIS spectrophotometer

The UV-Vis results show good absorbance in the UV-region and the energy absorption band gap was found with the help of a Tauc plot.

The UV–visible spectra of VO_2 (B) nanoplates are shown in Figure 4. From the figure, it is observed that the absorbance increases from minimum to maximum in the UV-region while in Visible and Near IR-region shows higher absorbance. The linear portions of the corresponding absorption coefficient data plot can be extrapolated to intersect the energy axes i.e. 'x' axis at α=0. The corresponding values of the energy data will give optical band gap of the synthesized samples.

The optical band gap, E_g, can be estimated from the following equation known as the tauc plot [42]. The optical energy gap was found to be 2.3eV, 3.1eV and 3.2 eV of sample 1, sample 2 and sample 3 respectively.

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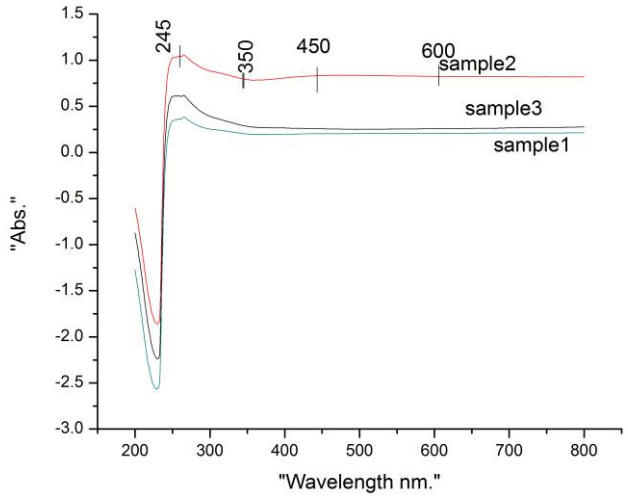

Fig 4: The figure above shows absorbance of the synthesized samples 1, 2 and 3 prepared by hydrothermal, low temperature method and microwave assisted solution based methods respectively, corresponding to the wavelengths of incident radiation.

Transmission **Electron Microscopy**

HRTEM images of hydrothermally treated samples show uniformly crystalline nanoparticles. Thus the average crystal size is of the order of 7-8 nm.

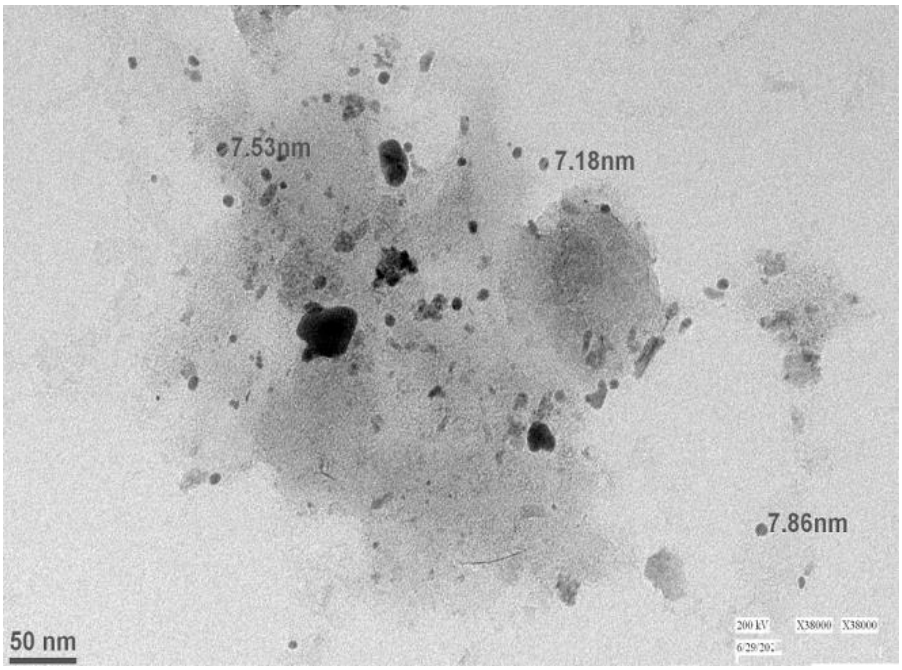

Fig. 5: Micrograph of Sample 1 confirming uniformity and nano size of particles.

Conclusions

In summary, VO_2 (B) nanoparticles were successfully synthesized via three different techniques. All three techniques can be used for synthesis of VO2 (B) phase at the nanoscale. However, for producing any material in a commercially viable way, the synthesis technique should be cheap, scalable and convenient to use. The hydrothermal technique can be used to prepare nanosized oxide samples in simple and straightforward steps as compared with other techniques. The autoclave provides a controlled environment to the synthesis process during hydrothermal treatment due to which uniformity and reproducibility in the final products' chemistry, size and morphology can be achieved. A small controlled change in the hydrothermal condition changes the morphology which affect the properties of the material such as the shape of crystals or the optical energy band gap. .In this way, it can be said that used technique is better as compared to others for synthesis of modern products with typical compositions and desired morphology.

References

[1] F. Wang, Y. Liu, and C. yan Liu, "Hydrothermal synthesis of carbon/vanadium dioxide core-shell microspheres with good cycling performance in both organic and aqueous electrolytes," *Electrochim. Acta*, vol. 55, no. 8, pp. 2662–2666, 2010.
[2] D. Johansson, "Examensarbete VO 2 films as active infrared shutters Daniel Johansson," *Master Thesis*, 2005.
[3] L. Mai *et al.*, "Nanoscroll buffered hybrid nanostructural VO2 (B) cathodes for high-rate and long-life lithium storage," *Adv. Mater.*, 2013.
[4] S. Li, G. A. Niklasson, and C. G. Granqvist, "Nanothermochromics : Calculations for VO 2 nanoparticles in dielectric hosts show much improved luminous transmittance and solar energy transmittance modulation," pp. 1–8, 2010.
[5] Y. Dwivedi, S. B. Rai, J. P. Singh, C. Lamsal, and N. M. Ravindra, "VANADIUM OXIDES FOR ENERGY AND SECURITY APPLICATIONS."
[6] H. M. Cele, "Synthesis of VO2 Nanostructures for Infrared Modulation Applications," *Dep. Phys. Eng.*, vol. Magister S, no. November, p. 123, 2009.
[7] H. J. Song *et al.*, "Enhanced Lithium Storage in Reduced Graphene Oxide- supported M-phase Vanadium (IV) Dioxide Nanoparticles," *Nat. Publ. Gr.*, no. April, pp. 6–13, 2016.
[8] J. Wang, C. Feng, Z. Sun, S. Chou, H. Liu, and J. Wang, "In-situ One-step Hydrothermal Synthesis of a Lead Germanate-Graphene Composite as a Novel Anode Material for Lithium-Ion Batteries," pp. 1–7, 2014.
[9] a. K. Prasad, S. Amirthapandian, S. Dhara, S. Dash, N. Murali, and a. K. Tyagi, "Novel single phase vanadium dioxide nanostructured films for methane sensing near room temperature," *Sensors Actuators B Chem.*, vol. 191, pp. 252–256, 2014.
[10] J. Maeng, T. W. Kim, G. Jo, and T. Lee, "Fabrication, structural and electrical characterization of VO2 nanowires," *Mater. Res. Bull.*, 2008.
[11] A. Pergament, A. Crunteanu, and A. Beaumont, "Vanadium Dioxide : Metal-Insulator Transition , Electrical Switching and Oscillations . A Review of State of the Art and Recent Progress," pp. 9–12, 2015.
[12] K. Y. Kang, "Fabrication and Electrical Properties of Pure VO 2 Phase Films," pp. 1–5.
[13] J. M. Honig, "Electrical Transitions in Metal Oxides *," vol. 13, 1982.
[14] C. L. N. M. Ravindra, "Optical properties of vanadium oxides-an analysis," no. February, pp. 6341–6351, 2013.
[15] T. Peterseim, M. Dressel, M. Dietrich, and A. Polity, "Optical properties of VO2 films at the phase transition: Influence of substrate and electronic correlations," *J. Appl. Phys.*, vol. 120, no. 7, p. 75102, 2016.
[16] A. Gon??alves *et al.*, "Smart optically active VO2 nanostructured layers applied in roof-type ceramic tiles for energy efficiency," *Sol. Energy Mater. Sol. Cells*, vol. 150, pp. 1–9, 2016.
[17] L. G. Socaciu, "Thermal energy storage with phase change material," *Leonardo Electron. J. Pract. Technol.*, 2012.
[18] P. Lyons, D. Arasteh, and C. Huizenga, "Window Performance for Human Thermal Comfort," 1999.
[19] M. C. Rao and K. Ramachandra Rao, "Thermal evaporated V2O5 thin films: Thermodynamic properties," *Int. J. ChemTech Res.*, 2014.
[20] B. T. Laboratories *et al.*, "Magnetic and Crystal Structure of Titanium Sesquioxide," vol. 130, no. 10, pp. 2230–2237, 1963.
[21] P. Kanoo, A. C. Ghosh, and T. K. Maji, "A vanadium (VO2+) metal-Organic framework: Selective vapor

adsorption, magnetic properties, and use as a precursor for a polyoxovanadate," *Inorg. Chem.*, vol. 50, no. 11, pp. 5145–5152, 2011.
[22] J. Liu, Q. Li, T. Wang, D. Yu, and Y. Li, "Metastable vanadium dioxide nanobelts: hydrothermal synthesis, electrical transport, and magnetic properties.," *Angew. Chem. Int. Ed. Engl.*, vol. 43, no. 38, pp. 5048–5052, 2004.
[23] L. Dai *et al.*, "F-doped VO2 nanoparticles for thermochromic energy-saving foils with modified color and enhanced solar-heat shielding ability.," *Phys. Chem. Chem. Phys.*, vol. 15, no. 28, pp. 11723–9, 2013.
[24] J. Zhou *et al.*, "VO 2 thermochromic smart window for energy savings and generation."
[25] M. Imada, A. Fujimori, and Y. Tokura, "Metal-insulator transitions."
[26] S. R. Popuri, M. Miclau, A. Artemenko, C. Labrugere, A. Villesuzanne, and M. Pollet, "Rapid hydrothermal synthesis of VO2 (B) and its conversion to thermochromic VO2 (M1)," *Inorg. Chem.*, 2013.
[27] J. Wang, C.-Q. Feng, Z.-Q. Sun, S.-L. Chou, H.-K. Liu, and J.-Z. Wang, "In-situ One-step Hydrothermal Synthesis of a Lead Germanate-Graphene Composite as a Novel Anode Material for Lithium-Ion Batteries."
[28] J. Ma, Y. Hou, K. Jia, B. Chen, and S. Zhang, "A paradoxical contraction appearing in Eu3+ doped vanadium dioxide (B) nanocrystal via hydrothermal process," *Mater. Lett.*, 2016.
[29] D. Li *et al.*, "Hydrothermal synthesis of Mo-doped VO2/TiO2 composite nanocrystals with enhanced thermochromic performance," *ACS Appl. Mater. Interfaces*, vol. 6, no. 9, pp. 6555–6561, 2014.
[30] J. H. Son, J. Wei, D. Cobden, G. Cao, and Y. Xia, "Hydrothermal synthesis of monoclinic VO2 micro- and nanocrystals in one step and their use in fabricating inverse opals," *Chem. Mater.*, 2010.
[31] R. Chen *et al.*, "Shape-controlled synthesis and influence of W doping and oxygen nonstoichiometry on the phase transition of VO 2," *Nat. Publ. Gr.*, 2015.
[32] Y. Zhang, J. Zhang, X. Zhang, Y. Deng, and Y. Zhong, "In fl uence of different additives on the synthesis of VO 2 polymorphs," vol. 39, pp. 8363–8376, 2013.
[33] Z. Ke-chao, C. Du-meng, and L. Zhi-you, "Soft-chemical synthesis and high-temperature electrochemical characteristics of VO 2."
[34] R. Bharathi, R. Naorem, and M. Umarji, "Metal–insulator transition characteristics of vanadium dioxide thin films synthesized by ultrasonic nebulized spray pyrolysis of an aqueous combustion mixture," *J. Phys. D. Appl. Phys.*, vol. 48, no. 30, p. 305103, 2015.
[35] Y. Ji *et al.*, "Role of microstructures on the M1-M2 phase transition in epitaxial VO 2 thin films," pp. 2–7, 2014.
[36] G. A. Horrocks, S. Singh, M. F. Likely, G. Sambandamurthy, and S. Banerjee, "Scalable Hydrothermal Synthesis of Free-Standing VO 2 Nanowires in the M1 Phase," 2014.
[37] X. Chen, J. Li, and Q. Lv, "Optik Thermoelectrical and optical characteristics research on novel nanostructured VO 2 thin film," *Opt. - Int. J. Light Electron Opt.*, vol. 124, no. 15, pp. 2041–2044, 2013.
[38] Z. Zhang *et al.*, "Thermochromic VO 2 Thin Films : Solution-Based Processing , Improved Optical Properties , and Lowered Phase Transformation Temperature," vol. 26, no. 8, pp. 10738–10744, 2010.
[39] T. Doping, "Decoupling the Lattice Distortion and Charge Doping Effects on the Phase Transition Behavior of VO 2 by Titanium," pp. 1–8, 2015.
[40] C. Cheng *et al.*, "Self-Assembly and Horizontal," no. 110, pp. 1–5, 2014.
[41] S. Hu *et al.*, "Optical properties of Mg-doped VO2: Absorption measurements and hybrid functional calculations," *Appl. Phys. Lett.*, vol. 101, no. 20, 2012.
[42] I. Mjejri, N. Etteyeb, and F. Sediri, "Mesoporous vanadium oxide nanostructures: Hydrothermal synthesis, optical and electrochemical properties," *Ceram. Int.*, 2014.
[43] J. Shin, H. Jung, Y. Kim, and J. Kim, "Carbon-coated V2O5 nanoparticles with enhanced electrochemical performance as a cathode material for lithium ion batteries," *J. Alloys Compd.*, vol. 589, pp. 322–329, 2014.
[44] L. D. Frederickson and D. M. Hausen, "Infrared Spectra-Structure Correlation Study of Vanadium-Oxygen Compounds.," *Anal. Chem.*, vol. 35, no. 7, pp. 818–827, 1963.
[45] C. Xiong, A. E. Aliev, B. Gnade, and K. J. Balkus, "Fabrication of Silver Vanadium Oxide and V 2 O 5 Nanowires for Electrochromics," *ACS Nano*, vol. 2, no. 2, pp. 293–301, 2008.
[46] M. Lankelma *et al.*, "A novel one-dimensional chain built of vanadyl ions and pyrazine-2,5-dicarboxylate.," *Dalton Trans.*, vol. 44, no. 25, pp. 11380–11387, 2015.