

Vanadium dioxide for energy conservation and energy storage applications: Synthesis and performance improvement



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HIGHLIGHTS

- Elaborated six chemical vapor deposition (CVD) methods to growth VO₂ pure phase.
- Discussed the optimum conditions for VO₂ pure phase growth for various CVD methods.
- Strategies to improve VO₂'s thermochromic and electrochemical performance.
- Future perspective to stimulate the research in energy saving and storage field.

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ABSTRACT

Vanadium dioxide (VO₂) is one of the most widely studied inorganic phase change material for energy storage and energy conservation applications. Monoclinic VO₂ [VO₂(M)] changes from semiconducting phase to metallic rutile phase at near room temperature and the resultant abrupt suppressed infrared transmittance at high temperature makes it a potential candidate for thermochromic smart window application to cut the air-condition usage. Meanwhile proper electrical potential, stable structure and good interaction with lithium ions make metastable VO₂ [VO₂(B)] an attractive material for fabrication of electrodes for batteries and supercapacitors. However, some long-standing issues have plagued its usage. In thermochromic application, high transition temperature (τ_c), low luminous transmittance (T_{lum}) and undesirable solar modulation ability (ΔT_{sol}) are the key problems, while in energy storage applications, short cycling lifetime and complex three-dimension microstructure are the major challenges. The common methods to produce VO₂ polymorph are physical vapour deposition (PVD), chemical vapour deposition (CVD), sol-gel synthesis, and hydrothermal method. CVD is an intensively studied method due to its ability to produce uniform films with precise stoichiometry, phase and morphology control. This paper reviews the various CVD techniques to produce VO₂ with controlled phases and the ternary diagram shows the relationship between film stoichiometry and various process conditions. The difference between the various CVD systems are commented and the process window to produce VO₂ are tabulated. Some strategies to improve VO₂'s performance in both energy conservation and energy storage applications are discussed.

1. Introduction

As the world population increasing, the energy demand of society increases rapidly. The world energy consumption in 2020 will increase to 53 billion kWh [1,2]. Because of the limited amount of conventional energy sources such as coal, crude oil and natural gas, the current

energy consumption practice has been proved as unsustainable. To fulfil the requirement of sustainability, approaches such as cutting off energy usage and exploring cleaner energy source have to be employed.

Energy saving in building is one of the important tasks in energy usage cutting off since building is one of the largest energy usage sectors. According to the report from United Nations, human-made

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Nomenclature

AACVD	aerosol assisted chemical vapour deposition
ALD	atomic layer deposition
APCVD	atmospheric pressure chemical vapour deposition
AR-layer	anti-reflecting layer
CVD	chemical vapour deposition
CNT	carbon nanotube
DLI-MOCVD	direct liquid injection metal-organic chemical vapour deposition
FESEM	field emission scanning electron microscope
ITO	indium tin oxide
HVAC	heating, ventilation and air conditioning

MFC	mass flow controller
MIT	metal insulator transition
MOCVD	metal-organic chemical vapour deposition
PECVD	plasma enhanced chemical vapour deposition
PVD	physical vapour deposition
SEM	scanning electron microscope
SPR	surface plasmon resonance
τ_c	transition temperature
TEM	transmission electron microscope
TEMAV	tetrakis[ethylmethylamido]vanadium
T_{lum}	luminous transmittance
VLS	vapour-liquid-solid
ΔT_{sol}	solar modulation ability

building consumes 40% of total primary energy requirement globally and emits 30% of annual carbon dioxide emission [3]. Within the energy usage in building, heating, ventilation and air conditioning (HVAC) applications use about 50% of total energy [4]. Based on these data, reducing energy consumption for HVAC becomes an important task for architect and engineer. The HVAC energy consumption can be reduced via both aggressive and passive ways such as improving the efficiency of air conditioning system, adding thermal insulating to the wall, using cooling roof, and installing smart window glazing [5–7]. Since the window is the most energy inefficient component in the building, regulation the heat through the window becomes an important consideration for designer and national standard [8,9]. Vanadium oxide (VO_2) is one of the phase change materials used as thermochromic smart window coating to cut off the energy consumption for regulating room temperature due to its near room temperature metal-insulator transition (MIT) and has attracted attention from academia and industry. When temperature increases above the transition temperature (τ_c), the material transits from insulator to metal and its lattice changes from monoclinic to rutile with a diminished transmittance in the near-infrared range [10]. Therefore, temperature dependent solar modulation can be triggered automatically. Based on the heat reflection and absorption effect from the metallic state of VO_2 , the building in warm-area (Cairo, Palermo and Rome) that employs VO_2 coated smart window shows an annual energy saving up to 10% [11]. Although $VO_2(M)$ is attractive as an energy conservation material, some limitations restrict its application: First, bulk $VO_2(M)$ has a τ_c at $\sim 68^\circ\text{C}$, which is too high for room-temperature applications. Secondly, the integrated luminous transmission (T_{lum}) for $VO_2(M)$ is only $\sim 40\%$ with a noticeable magnitude of solar modulation (ΔT_{sol}) $< 20\%$ which is insufficient for windows coating applications [12]. Nanothermochromism [13–15], controlled porous films [16], moth-eyed nanostructure [17], multi-layered antireflective over-coated films [18] and gridded structures [19–21] as shown in Fig. 1 have been investigated to address those issues. The organic [22] and hybrid structure [23,24] show superior T_{lum} and ΔT_{sol} , however they suffer from low durability and the translucent state at a high temperature, which is not favourable for window applications. In inorganic VO_2 , the performance varies significantly due to the difficulty to control the crystallinity [25], uniformity, morphology [26] and phases because of its rich valence [27,28].

On the other hand, although the cleaner energy such as solar energy and wind energy have been successfully commercialised, it is still very far from fully replacing the fossil fuel because of several limitations of the cleaner energy. For example, the photovoltaic panel can only generate electrical power during the daytime, and the amount of electricity generated by wind turbine is not stable since the speed of wind changes with time. Those issues prevent the large-scale application of solar and wind energy in everyday life [29]. Moreover, the development of electric vehicles based on the requirement to get rid of fossil fuel raises higher demand to the large capacity energy storage device [30].

Meanwhile, energy storage technology is also used to harvest the wasted kinetic energy from vehicle and large machine [31,32]. Under this circumstance, metastable VO_2 [$VO_2(B)$] attracts attention in the energy storage area as battery and supercapacitor electrode materials and supercapacitor materials. $VO_2(B)$ presents the advantage of having a proper electrode potential, which is desirable for batteries and supercapacitors [33]. Moreover, the unique tunnel structure of $VO_2(B)$ allows lithium ion intercalate and deintercalate in reversible Li-ion battery [34]. Meanwhile, $VO_2(B)$ has the outstanding resistance to the lattice shearing during charging cycling because of its increased edge shearing [35]. Lastly yet importantly, compared with the current cathode material in lithium battery such as $LiCoO_2$, the vanadium based cathode has lower cost due to the abundance in nature [36]. Since the morphology of electrode component has a significant influence on electrochemistry performance [37], a batch of one-dimension (1D) and two-dimensions (2D) structure such as nanorod [38], nanowire [39], nanobelt [40] and nanoparticles [41] have been produced. However, those structures suffer from poor cycling stability [42]. Three-dimensional (3D) microstructures such as flower-like structure [43], nanothorn hollow microsphere [42] and urchin-like structure [44] have been reported to exhibit superior cycling stability over 1D and 2D nanostructures because of the porous and rigid 3D structures. Meanwhile, several groups [45,46] proved that carbon coating on electrode effectively improved electrode cycling stability. Despite the advances of these two ideas, there are still have some limitations. First, the thick carbon coating is not preferred in supercapacitor and battery electrodes as it hinders the diffusion kinetics of Li-ion and slows down the charge/discharge rate [47], which eliminates the advantage of tunnel structure in $VO_2(B)$ crystal. Second, the current commonly used method such as hydrothermal process is not good at controlling film thickness precisely.

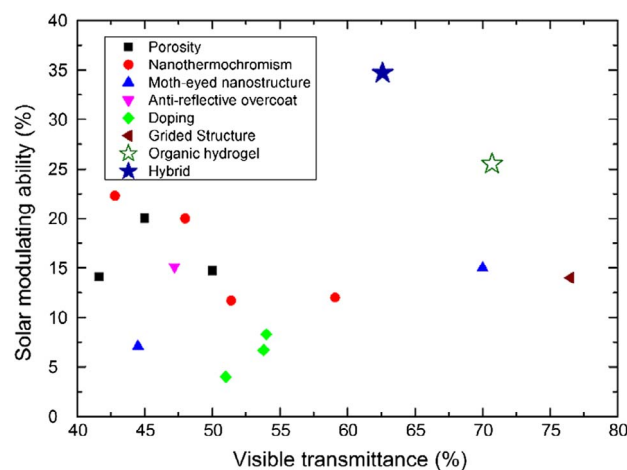


Fig. 1. Thermochromic performance of film produced by the various methods. Adapted from Ref. [24] with permission from Wiley.

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