Vanadium Oxide Nanoparticles Doped Polymer to Modulate Thermal Emissivity

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Abstract. Vanadium oxide (VO₂) finds a wide range of applications owing to its excellent reversible phase change properties. We demonstrate a method for doping a polymer with VO₂ nanoparticles towards realizing a thermal emissivity modulation device, which is expected to supplement the conventional preparation of VO₂ film layers using magnetron sputtering, vapor deposition, and such techniques which are relatively cumbersome and expensive. The comparison of thermal emissivity modulation ability of VO₂ film membrane structure on silicon substrate obtained by magnetron sputtering and pressed tablet sample obtained from VO₂ nanoparticles reveals that the latter also demonstrates substantial thermal emissivity modulation ability. Furthermore, the emissivity of this fabricated PDMS-VO₂ blended sample can change from 0.90 to 0.71 in a heating test. This provides us a new technique to fabricate a scalable, cost effective, and widely applicable thermal emissivity modulation device.

1. Introduction
Vanadium oxide (VO₂) has received much attention because of its excellent reversible insulator-to-metal transition (IMT) properties [1]. The IMT temperature of vanadium oxide is approximately 68 °C. When IMT occurs, the values of optical constants of VO₂ change drastically. The IMT process of VO₂ can be regulated electrically, thermally, or optically [2]. Additionally, the IMT of VO₂ being reversible, VO₂ can regain the insulated state when the temperature the sample is decreased [3]. Because of this reversible IMT effect of VO₂, it holds a great promise to be utilized in a wide range of applications, such as phase change switches, infrared stealth devices, environmentally friendly smart windows, and emissivity modulation devices [4].

Currently, there exist multiple ways to prepare VO₂ films, such as molecular beam epitaxy, magnetron sputtering, vapor deposition (CVD), pulsed laser deposition (PLD), physical vapor deposition (PVD), atomic layer deposition, and sol-gel methods, among others [5]. However, these methods have some drawbacks, such as scalability, cost effectiveness, and necessitating an annealing process which constraints the use of heat-resistant substrates.

In this regard, we propose to mix VO₂ nanoparticles with some typical polymers which demonstrate state transition properties towards achieving a scalable, cost effective, and relatively easier fabrication method to realize a device showing substantial thermal emissivity modulation. The polymers form a large family and have a wide range of applications in our daily life. A typical polymer has some special properties, for instance polydimethylsiloxane (PDMS) [6] and polymethyl methacrylate (PMMA) remain in fluid state at room temperature and gets cured when heated [7]. Also, Poly (vinyl alcohol) (PVA) has a desirable property that it can be dissolved in deionized water [7]. When the solvent is evaporated, we obtain a complete PVA film. A more common way is heating the
polymer to its melting point and mixing nanoparticles and thereafter cooling it in a mold [8]. Because of the special IMT effect of VO$_2$ and the state transition properties of these polymers, a mix of VO$_2$ nanoparticles and one of these polymers could pave a new technique to realize a scalable, cost effective, and convenient way to achieve thermal emissivity modulation.

2. Method

2.1. Material and Sample Preparation
Polydimethylsiloxane (PDMS) and VO$_2$ nanoparticles (purity ~ 99.5% and diameter ~ 200 nm) are acquired for this study. The sample preparation broadly involves four steps. First, 0.3g VO$_2$ nanoparticles is paved on an aluminum box (diameter 30 mm). Second, 4g PDMS elastomer is mixed with 0.4g curing agent. Third, PDMS mixture is poured to the aluminum box. Thereafter, the sample is placed in a vacuum chamber for 2 hours to remove air bubbles in the sample. Finally, the box is placed on a hot table and heated at 100 ℃ for 1 hour to solidify the PDMS. In this way, we get PDMS-VO$_2$ blended sample (PVB).

2.2. Instrumentation
IR-camera (operating wavelength 8-14 µm) and Fourier Transform Infrared Spectrometer (FTIR) are utilized for characterization of the prepared samples.

2.3. Principle Explanation
VO$_2$ undergoes a phase transition when the temperature is increased. The optical constants of VO$_2$ change drastically, and as a result, its optical properties change significantly (see figure 1). A significant difference in refractive index and extinction coefficient of VO$_2$ in insulated state and metallic state can be observed.

![Figure 1](image_url)

Figure 1. The refractive index $n$ and extinction coefficient $k$ of VO$_2$ in both insulated state (I) and metallic state (M) record from reference [9].

When the VO$_2$ film change from insulated state to metallic state, we measure the reflection spectrum of magnetron sputtered VO$_2$ film (silicon substrate and 200 nm VO$_2$) and VO$_2$ pressed tablet sample (manufactured through the VO$_2$ nanoparticles pressed into tablets) by using FTIR. For a structure with flat surfaces, it obeys the following formula
\[ \alpha + \rho + \tau = 1. \]  
(1)

where \( \alpha \), \( \rho \), and \( \tau \) are the absorption, reflection, transmission rates of the sample, respectively. The \( \tau \) value being almost zero for the test samples, the simplified formula becomes

\[ \alpha + \rho = 1. \]  
(2)

According to Kirchhoff’s law, \( \varepsilon = \alpha \), where \( \varepsilon \) is the emissivity of the sample. The emissivity of both magnetron sputtered VO\(_2\) film and VO\(_2\) pressed tablet samples are measured by FTIR (see figure 2(a)). It can also be observed that both magnetron sputtered VO\(_2\) film and VO\(_2\) pressed tablet samples demonstrate significant emissivity difference - the difference of emissivity corresponding to the insulated state and the metallic state of the samples (figure 2(b)). It demonstrates that VO\(_2\) nanoparticles can achieve emissivity modulation. Meanwhile, it can also be observed that the membrane system structure of VO\(_2\) film has a stronger emissivity modulation effect, twice as much as pressed tablet sample.

![Figure 2](image.png)

**Figure 2.** Comparison of the emissivity of magnetron sputtered VO\(_2\) film (blue lines) and VO\(_2\) pressed tablet sample (red lines) in insulated state and metallic state. (a) Measured emissivity spectrum of the two samples in the insulated state (solid lines) and metallic state (dashed lines). (b) The emissivity change corresponding to the IMT is plotted for the two samples.

### 3. Experiment and Results Discussion

To record the infrared images, we put the PVB on a hot table and heat the PVB from room temperature to 90 °C. During the heating time, the change process of the mid-infrared signal over time is recorded by IR-camera (8-14 \( \mu \)m). Figure 3(a) shows the visible image of PVB. We stick a black tape on the surface of PVB as shown in figure 3(b) area 1. The emissivity of a black tape (\( \varepsilon_1 = 0.98 \)) approximately resemble that of an ideal black body, so it can be regarded as a calibration reference. Area 2 is the PVB surface. We record the average infrared temperature of each area to characterize the thermal emissivity variation. Figure 3(b) shows the infrared image of PVB at 40 °C, and figure 3(c) shows the infrared image of PVB at 90 °C. Comparing figure 3(b) with figure 3(c), we conclude that the emissivity of the PVB decreased due to the IMT of VO\(_2\). Figure 3(d) and (e) show the average infrared temperature of each area and the emissivity change of PVB over time.
Figure 3. The thermal emissivity modulation function of PVB. (a) The visible image of a PVB. (b-c) Comparison of emissivity (under 40 °C and 90 °C) of PVB (d) Infrared temperature change over time. (e) The emissivity of PVB change over time.

According to the Stefan-Boltzmann law,

\[ M(T) = \sigma T^4. \]  

(3)

The emissivity of PVB \( \varepsilon_p \) can be calculated by the following simplified formula given by

\[ \varepsilon_p = \varepsilon_r \frac{T_p^4}{T_r^4}, \]

(4)

where \( \varepsilon_p \) is the emissivity of PVB, \( \varepsilon_r \) is the reference emissivity of black tape, \( T_p \) is the infrared temperature of PVB, and \( T_r \) is the infrared temperature of black tape.

4. Conclusion

In summary, we demonstrate the insulator-to-metal transition effect of the VO\(_2\) pressed tablet sample fabricated by combining VO\(_2\) nanoparticles with PDMS and compare its thermal emissivity modulation ability with VO\(_2\) films fabricated by magnetron sputtering. The recorded IR temperature change of the PDMS-VO\(_2\) blended sample over time demonstrates its excellent thermal emissivity modulation ability. However, the thermal modulation ability is observed to be relatively weaker compared to the VO\(_2\) film fabricated by magnetron sputtering technique. The reason is attributed to the high emissivity of PDMS polymer, which hinders the thermal emissivity modulation ability of the PDMS-VO\(_2\) blended sample to some extent. It can be speculated that if a polymer with low emissivity in 8-14 µm range can substitute PDMS, a better performance in terms of thermal emissivity modulation can be achieved. The use of this VO\(_2\) nanoparticle doped polymer provides a new avenue for comparatively easier fabrication of a scalable and cost effective thermal emissivity modulation device.
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