A FACILE PREPARATION OF VO2-PVP NANOCOMPOSITE COATING FOR SMART WINDOW APPLICATION WITH IMPROVED VISIBLE TRANSMITTANCE

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Abstract

Vanadium dioxide (VO2) is a promising smart window coating due to its thermochromic ability. However, its practical application is still on hold due to some limitations. For instance, a thin film coating of VO2 suffers from low visible transmittance (Tvis). A new and simple technique to solve this restriction is by embedding nanoparticles onto film. Hence, this paper presents a preparation of nanocomposite coating derived from hydrothermally synthesized VO2 with improved Tvis. Using polyvinylpyrrolidone (PVP) as host matrix, nanostructured VO2 is dispersed onto a glass sample via a spin coating process. X-ray diffraction (XRD) scan showed the presence of monoclinic VO2 in the film. Surface analysis of the sample was carried out using atomic force microscopy (AFM). Based on the results, the roughness of the scanned area (1.5x1.5 μm2) has a mean height (Sa), and root mean square height (Sq) of 3.94 nm and 2.73 nm, respectively. Finally, calculation of the optical properties of the sample was done with the aid of a UV-vis spectrophotometer. Accordingly, the prepared nanocomposite film has a Tvis of 79.81% which is significantly higher than a thin film sample (Tvis = 65%).

Keywords: Nanocomposite, Surface analysis, Thermochromic, Vanadium dioxide

Introduction

Energy consumption in the built environment is increasing, primarily to satisfy the demands for air conditioning, ventilation, and lighting (Granqvist, Lansaker, Mlyuka, Niklasson & Avendaño, 2009). However, a vast portion of this energy is lost through windows or glazed areas (Long & Ye, 2014). Hence, there is a need to improve the properties of windows for it to be more energy efficient. One way to achieve this is by coating windows with a thermochromic material (Saeli, Piccirillo, Warwick & Binions, 2013), that is, a material that can control the amount of heat passing through it (Kamalirazestani, Saidur, Mekhilef & Javadi, 2013).

Vanadium dioxide (VO2) is among the compounds that exhibit thermochromism as it undergoes a reversible metal-semiconductor transition (MST) at critical temperature (Tc) of 68°C (Goodenough, 1971). Below Tc, VO2 is semiconducting and is transparent to infrared (IR); whereas, above Tc, it shifts to metallic phase with IR reflecting ability (Morin, 1959). Hence, a considerable number of researches have been carried out to fabricate VO2 thin films for real-world application. Several techniques have been proposed including chemical vapor deposition (Vernardou, Pemble & Sheel, 2006; Piccirillo, Binions & Parkin, 2008), physical vapor deposition (Chae, Youn, Kim & Maeng, 2003; Maaza, et al., 2000), sputtering system (Chen, Lai, Dai, Ma, Wang & Yi, 2009; Xu, et al., 2010), and sol-gel method (Dachuan, Niankan, Jingyu & Xiulin, 1996; Wang, Magdassi, Mandler & Long, 2013). However, its practical application has long been hampered by some restrictions. Among these is its low visible-light transmittance (Tvis) (Wang, Liu, Kong, Long, Jiang & Yu, 2016; Yu, Nam, Lee & Boo, 2016).

A facile and innovative way to improve Tvis is by using VO2 composite coating (Li, Niklasson & Granqvist, 2012). In this method, VO2 nanoparticles are embedded onto a substrate with a polymeric host matrix (Valmatt & Gavarri, 1994) Polymers such as polyethylene (PE), polyurethane (PU), polyvinylphenol (PVP), and polyvinyl alcohol (PVA) have been used in previous researches (Alfred-Duplan, Musso, Gavarri & Cesari, 1994; Chen, et al., 2013; Shen, et al., 2014; Madida, et al., 2014). In this study, we report on the use of another polymer, polyvinylpyrrolidone (PVP), as a new host matrix. Also, we present the preparation of nanocomposite film that is derived from hydrothermally prepared VO2. Furthermore, phase, morphology, topography, and optical property analyses were carried out to investigate the properties of the acquired samples.
Methods

All chemicals used in this experiment were of analytical grade and used without further purification. Vanadium pentoxide (V2O5) powder with a mass of 1.875 g was poured into a beaker containing 150 mL deionized water. The solution was mixed vigorously using a magnetic stirrer. Afterward, 3.4024 g of oxalic acid (H2C2O4) was poured into the same beaker to reduce the oxidation state of V2O5. The stirring continued until the solution turned dark blue-green. Then, it was transferred into a 240-mL Teflon-lined steel autoclave and placed inside an electric oven, where it was heated at 180 °C for 24 h. After cooling naturally, the blue-black precipitate was collected, centrifuged, rinsed with water and ethanol several times, and dried at 60°C overnight. Since the acquired VO2 powder was in a metastable state, post-heating treatment was done. The sample was placed in a tube furnace and annealed at 650 °C for two h under a nitrogen atmosphere with a heating rate of 10°C/min.

The prepared VO2 nanoparticles were dispersed in ethanol under magnetic stirring for 10 minutes. Meanwhile, polyvinylpyrrolidone (PVP K15) was dissolved in a separate beaker containing ethanol. The mass ratio of VO2 and PVP was 1:1 while both the VO2/ethanol and PVP/ethanol had concentrations of 2%. Then, the solutions were mixed and treated ultrasonically for 15 min. This was done to ensure good homogeneity and minimize clustering of nanoparticles. Before the coating stage, a glass substrate with dimensions of 1.5cm x 1.5cm x 1mm was washed with ethanol. Then it underwent ultrasonic treatment for 15 min and was dried in ambient condition. Finally, the suspension was embedded onto the cleaned substrate using a spin-coating device at a speed of 1500 rpm for 30s. Lastly, it was dried in an oven at 80°C for 1h.

Analyses on the phase and crystal structure of the prepared samples were done by X-ray diffraction (XRD, Xpert Pro Panalytical Philips DY 1861) in the scanning range (2θ values) between 20° and 80°. The morphology of the hydrothermally synthesized VO2 was examined by field emission scanning electron microscope (FESEM, JEOL-JSM7600F). Furthermore, the thermo-chromatic property of the nanostructured sample was studied using differential scanning calorimetry (DSC, DSC822, Mettler Toledo). This was done by calculating heat flow on the sample as the temperature was increased from 30°C to 200°C and then decreased back to 30°C. For the composite coating sample, the thickness was measured by stylus profilometer (Ambios XP 200), while its surface topography was analyzed using atomic force microscopy (AFM, Dimension Edge, Bruker) in tapping mode. Finally, the optical properties of the samples were measured using UV-visible-NIR spectrophotometer (Shimadzu UV-3600) in the wavelength range of 280-1100 nm at room temperature. For comparison purposes, uncoated glass and the VO2-thin film prepared via the sol-gel method were also scanned.

Results and Discussion

The thermodynamically stable phase of VO2 was successfully synthesized as displayed in the diffractogram in Fig. 1. All peaks can be matched with the monoclinic VO2 of space group P21/c with ICSD code 98-007-8277. Narrow peaks with high intensity were observed which correspond to better crystallinity. As shown in the FESEM image in Fig. 2, the as-prepared VO2 consists of spherical and oblate nanostructures with a diameter as small as 100 nm. Moreover, DSC results showed that the sample undergoes phase transition temperatures at 69.7°C and 62.59°C for heating and cooling directions, respectively. This corresponds to average Φc of 66.15°C and hysteresis of 7.11. Also, its average enthalpy of 40.7 J/g is similar to the value for bulk VO2 (Chen et al., 2017), which implies good phase change strength. Indeed, these low hysteresis and high enthalpy indicate good thermo-chromatic behavior. The DSC curve is illustrated in Fig. 3.

![Figure 1. XRD scan of the prepared VO2.](image-url)
Figure 2. FESEM image of the synthesized VO₂.

Figure 3. DSC curve of the VO₂ nanopowder.

The presence of VO₂ in the composite coating can be seen in the XRD scan in Fig. 4. The peaks matched the XRD pattern of the as-prepared VO₂ nanoparticles, albeit with decreased intensity. Understandably, this may be caused by a decreased amount of particles dispersed onto the film. The crystallite size, $D$, of the samples was calculated using the Scherrer formula (Soltane & Sediri, 2014),

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where $\lambda$ is the X-ray radiation wavelength ($\lambda_{Cu} = 1.5418 \text{ Å}$), $\beta$ is the peak width at half maximum, and $\theta$ is the Bragg angle. Accordingly, the measured values of $D$ for the VO₂ in nanopowder and composite forms were 22.5 nm and 225.1 nm, respectively. This indicated the occurrence of agglomeration of nanoparticles during the preparation of the composite coating.

Figure 4. XRD patterns of the samples.
In addition, the thickness of the composite film as measured by a mechanical profilometer was 70 nm. Fig. 5 shows the 3D AFM scan of the composite coating, with dimensions of 1.5x1.5 μm², where dispersed VO2 onto PVP and glass substrate can be seen. The measured values of the roughness mean height (Sa) and root mean square height (Sq) of the sample’s scanned area was 3.94 nm and 2.73 nm, respectively. The inset in Fig.5 is a zoomed section of the image in 2D, which displays a clustered VO2 particle with a maximum height of 26 nm and width of 206 nm.

![3D AFM image of the VO2-PVP composite. Inset: a 2D image of a section showing](image)

Results of the UV-vis spectrophotometer scan of the samples, at room temperature, can be seen in Fig. 6. From the acquired data, visible transmittance (Tvis) and solar modulation ability (Tsol) were calculated using the following equation (Dai et al., 2013),

$$T_i = \frac{\int \phi_i(\lambda)T(\lambda)d\lambda}{\int \phi_i(\lambda)d\lambda},$$  \hspace{1cm} (2)

where i stands for ‘vis’ or ‘sol’, ϕvis is the standard luminous efficiency function for the photopic vision of human eyes (Wyszecki & Stiles, 2000), ϕsol is the solar irradiance spectrum for air mass 1.5 (American Society for Testing and Materials, 2013), T is transmittance, and λ is wavelength, which ranges from 390 to 780 nm for Tvis and from 280 to 1100 nm for Tsol.

![Transmittance spectra of the samples.](image)

Accordingly, the measured value of \(T_{vis}\) for the VO2-PVP composite, which is at 79.81%, exceeded that of the VO2-thin film (64.89%). Indeed, this value is closer to that of an uncoated glass sample, which has a measured \(T_{vis}\) of 91.19%. Also, an increase in \(T_{sol}\) was observed with the composite sample having a value of 77.85% while the thin film sample has 59.97%. These improved optical properties indicate the potential practical use of nanocomposite coating as a smart window material. The measured values are summarized in Table 1.
Table 1. Measured optical properties of uncoated and coated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>$T_{si}$ (%)</th>
<th>$T_{sol}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated glass</td>
<td>-</td>
<td>91.19</td>
<td>90.68</td>
</tr>
<tr>
<td>VO$_2$-thin film</td>
<td>50</td>
<td>64.89</td>
<td>59.97</td>
</tr>
<tr>
<td>VO$_2$-PVP composite</td>
<td>70</td>
<td>79.81</td>
<td>77.85</td>
</tr>
</tbody>
</table>

Conclusions

Thermochromic VO$_2$ was successfully synthesized via the hydrothermal method with post-annealing treatment. The synthesized sample exhibited good crystallinity and spherical nanoparticles based on the XRD and FESEM scans, respectively. It also displayed the phase transition at $T_c = 66.15^\circ$C with low hysteresis and high enthalpy, which indicate good thermochromic behavior. Meanwhile, effective dispersion of the as-prepared VO$_2$ onto a glass substrate, with PVP as host matrix, was achieved based on the XRD diffractogram of the composite coating. AFM image of this sample further validated the finding as embedded nanoparticles can be seen onto the substrate. Measurements of the sample’s scanned area resulted in roughness mean height ($S_a$) and root mean square height ($S_q$) of 3.94 nm and 2.73 nm, respectively. More significantly, optical property analysis showed that the VO$_2$-PVP composite coating has a visible transmittance of 79.81%, which is higher compared to thin film coated sample. Indeed, this result suggests that the nanocomposite coating has great potential for real-world application.

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References


