Synthesis of Tungsten-Doped Vanadium Dioxide Using a Modified Polyol Method Involving 1-Dodecanol

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Abstract: The doping of tungsten into VO 2 (M) via a polyol process that is based on oligomerization of ammonium metavanadate and ethylene glycol (EG) to synthesize a vanadyl ethylene glycolate (VEG) followed by postcalcination was carried out by simply adding 1-dodecanol and the tungsten source tungstenoxytetrachloride (WOCl 4 ). Tungsten-doped VEGs (W-VEGs) and their calcinated compounds (W x VO 2 ) were prepared with varying mixing ratios of EG to 1-dodecanol and WOCl 4 concentrations. Characterizations of W-VEGs by powder X-ray diffraction, differential scanning calorimetry, scanning electron microscopy, and infrared and transmittance spectroscopy showed that tungsten elements were successfully doped into W x VO 2 , thereby decreasing the metal-insulator transition temperature from 68 down to 51 ◦C. Our results suggested that WOCl 4 variously combined with 1-dodecanol might interrupt the linear growth of W-VEGs, but that such an interruption might be alleviated at the optimal 1:1 mixing ratio of EG to 1-dodecanol, resulting in the successful W doping. The difference in the solar modulations of a W 0.0207 VO 2 dispersion measured at 20 and 70 ◦C was increased to 21.8% while that of a pure VO 2 dispersion was 2.5%. It was suggested that WOCl 4 coupled with both EG and 1-dodecanol at an optimal mixing ratio could improve the formation of W-VEG and W x VO 2 and that the bulky dodecyl chains might act as defects to decrease crystallinity.

Keywords: vanadium oxide; thermochromic; nanoparticles; tungsten doping; smart windows

1. Introduction

Smart windows that use the thermochromic property of vanadium dioxide (VO 2 ) have been highlighted as a promising energy saving technology due to their selective control over the transmission of heat rays that enhances energy saving efficiency [1]. At 68 ◦C or below, VO 2 has a monoclinic structure (M) with a semiconducting property, and at temperatures above 68 ◦C, its crystal structure is transformed to a tetragonal rutile structure, accompanying a change in its electrical property from semiconducting to metallic [2]. This metal-insulator transition (MIT) enables VO 2 to selectively reflect near-infrared light (NIR) due to its metallic property above its MIT temperature while transmitting visible light [3]. To practically apply the thermochromic property of VO 2 to smart windows that can control sunlight transmission at room temperature, decreasing the MIT temperature of VO 2 down to around room temperature is very much required. The doping of VO 2 (M) with tungsten (W) atoms has been a promising route for reducing the MIT temperature of VO 2 (M) [4–7]. When tungsten atoms are doped to the VO 2 , it is expected that the original V 4+ -V 4+ pairs in VO 2 (M) are converted to V 3+ -V 4+ and V 3+ -W 6+ pairs by electron donation from W to the neighboring V ions. As a result,
the concentration of free electrons is increased via electron donation, and the monoclinic structure is distorted due to the insertion of larger doped $W^{6+}$ ions with an ionic radius of 64 pm than $V^{4+}$ ions with an ionic radius of 49.5 pm. Thus, the MIT temperature of pristine $VO_2$ is decreased, making $W_xVO_2$ (M) an ideal candidate for thermochromic window materials as it can reflect NIR at room temperature while transmitting visible light [8,9].

A variety of methods, including hydrothermal synthesis with an autoclave at a high pressure [10], chemical vapor deposition (CVD) [11], sputtering [12,13], and ion implantation [14], have been utilized to synthesize $W_xVO_2$ (M). However, these methods require complicated experimental parameter controls or special devices, thereby restricting the extension of these methods to large-scale production at a low cost. Thus, it is highly necessary to develop a convenient process that utilizes atmospheric pressure in air at a low processing temperature. A candidate method for resolving these issues is the thermolysis of vanadyl glycolate to synthesize $VO_2$ (M) [15,16]. In this method, an alcohol with two or more hydroxyl groups and high boiling points, such as ethylene glycol (EG) with a boiling point of 197 °C, is mixed with a cheap vanadium precursor, such as ammonium metavanadate ($NH_4VO_3$), and the resulting solution mixture is heated over 160 °C in atmospheric air followed by thermolysis of precipitates at a low pyrolytic temperature of 200 °C to produce $VO_2$ (M) (Scheme 1). In this polyol method, EG works as a stabilizer that limits particle growth and prevents aggregation [17], as a coupling agent that can further lead vanadyl ethylene glycolate (VEG) to oligomer with a repeat unit of VO(OCH$_2$CH$_2$O) [18], and as a reducing agent when the VEG is calcinated [19]. The crystal structure of VEG can also be depicted by the one-dimensional chain of the $VO_5$ square pyramids in the VO(OCH$_2$CH$_2$O) structure by edge sharing (Scheme 1) [19]. When using this method to make VEG, special devices are not required, and subsequent calcination can be carried out via a conventional sintering process, thereby suggesting its possibility for mass production at a low cost. Although the polyol method shows great potential for the facile synthesis of $W_xVO_2$, it is difficult to find reports about the polyol method being applied to synthesize $W_xVO_2$ nanoparticles. This lack of research seems to be because a special synthesis for tungsten precursors that can be coupled within VEG is necessary or because the insertion of the large $W^{6+}$ ions into the monoclinic $VO_2$ (M) at an atmospheric pressure is difficult. Thus, the synthesis of $W_xVO_2$ using the polyol method via thermolysis in atmospheric air remains challenging.

![Scheme 1](image_url)

**Scheme 1.** (a) Reaction for the preparation of $VO_2$ (M) via a polyol method and (b) a schematic illustration of the W-VEG synthesis and calcination.
In this study, we present a modified polyol method using 1-dodecanol as an additive to synthesize $W_xVO_2$ (M). 1-Dodecanol has a boiling point of 259 °C, which is high enough for the polyol method, and can act as both the solvent and capping agent, as shown in inorganic nanoparticle synthesis [20]. Unlike the original polyol method, we found that tungsten could be doped into VO$_2$ (M) with the addition of 1-dodecanol, thereby reducing the MIT temperature of the resulting $W_xVO_2$ (M). We investigated the influence of the mixing ratios of EG and 1-dodecanol and the amounts of tungsten precursor on the synthesis of $W_xVO_2$. Our results suggest a procedure to dope tungsten into VO$_2$ (M) via the polyol method.

2. Materials and Methods

2.1. Materials

NH$_4$VO$_3$ and tungsten(VI) oxytetrachloride (WOCl$_4$) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). EG and 1-dodecanol were purchased from Alfa Aesar (Lancashire, United Kingdom). Ethanol was obtained from SamChun Pure Chemicals Co. (Seoul, South Korea). All the reagents used in this study were used as received.

2.2. Synthesis

To first synthesize tungsten-doped VEG (W-VEG), NH$_4$VO$_3$ (1.17 g, 10 mmol), 1-dodecanol (33.17 g, 17.8 mmol), and EG (11.05 g, 17.8 mmol) were added to a three-necked round-bottom flask and mixed with stirring. To this mixture solution, a pre-determined amount of WOCl$_4$ (0.094 g [0.277 mmol, 2.77 mol% to NH$_4$VO$_3$], 0.188 g [0.553 mmol, 5.53 mol%), and 0.377 g [1.109 mmol, 11.08 mol%]) was added, and the resulting reaction mixture was heated to 160 °C at a ramping rate of 5 °C/min and stirred for 2 h. Then, the mixture with a purple color was naturally cooled down to room temperature. The precipitate was collected by centrifuging the solution at 8000 rpm for 15 min to remove the excess 1-dodecanol and EG. The collected purple powder was washed with ethanol, filtered to obtain W-VEG powder, and dried in a vacuum for 24 h at room temperature.

The W-VEG powder was calcinated at 200 °C for 1 h in a box furnace in atmospheric air to become $W_xVO_y$ (M). After cooling to room temperature, $W_xVO_y$ (M) was calcinated again at 700 °C (10 °C/min) for 1 h in a tube furnace in a vacuum to obtain $W_xVO_y$ (M).

2.3. Characterization

The crystal structures of the $W_xVO_y$ (M) were verified by an X-ray diffractometer (XRD, Bruker-AXS NEW D8 Advance, Billerica, MA, USA). The MIT behaviors of the $W_xVO_y$ (M) were investigated using a differential scanning calorimeter (DSC Q-600; TA Instruments, New Castle, DE, USA) for analysis in the range −20–130 °C at a heating rate of 10 °C/min. Morphological observations of the nanostructures were conducted on a field-emission scanning electron microscope (FE-SEM; SIGMA, Carl Zeiss, Germany). The thermochromic properties of $W_xVO_y$ (M) were measured using UV-Vis-NIR spectroscopy (V-770, JASCO, Tokyo, Japan) in the range of 300–2500 nm. Before measuring the UV-Vis-NIR spectra, the $W_xVO_y$ (M) powder (0.02 g) was added in 5 mL of ethanol, and the solution was dispersed for 1 h under ultrasonication to make the suspension and placed in a quartz cell with 1 mm light path. The FT-IR spectra were recorded using a high-vacuum FT-IR spectrometer system in a spectral range of 4000 to 400 cm$^{-1}$ (Vertex 80V, operated by the Korea Basic Science Institute at Busan, Bruker Co., Billerica, MA, USA). KBr pellets that were prepared with 1 mg of samples and 15 mg of KBr were used for measurements in a vacuum. The compositions of $W_xVO_y$ were determined by using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES; Jobin Yvon Ultima2, operated by the Korea Basic Science Institute at Seoul; HORIBA, Edison, NJ, USA).
3. Results and Discussion

We used WOCl₄ as a tungsten precursor to synthesize WₓVO₂ (M) via the polyol method based on ammonium metavanadate and EG because WOCl₄ could be readily combined with EG via an exothermic reaction between WOCl₄ and hydroxyl groups that make byproducts of HCl. Thus, one might expect that WOCl₄ combined with EG participates in the formation of VEG, thereby resulting in the insertion of tungsten atoms into VO₂ (M) during calcination. However, when 2.77 mol% of WOCl₄ to NH₄VO₃ was added into the reaction mixture of ammonium metavanadate and EG at the 1:0 mixing ratio of EG to 1-dodecanol, the final product gained after calcination did not show a highly crystalline structure in its XRD pattern, as shown in Figure 1a. Additionally, the XRD pattern was not matched with that of VO₂ (M). This result can be ascribed to the incomplete synthesis of linear VEG via a condensation reaction between NH₄VO₃ and EG because WOCl₄ with four reactive W-Cl functionalities to EGs can interrupt the formation of the linear VEG.

![Figure 1](attachment://image.png)

Figure 1. (a) XRD patterns and (b) DSC thermograms of tungsten-doped vanadium oxides obtained with varying molar mixing ratios of EG to 1-dodecanol at 1:0, 1:0.5, 1:1 and 1:2.

We presumed that the simple addition of 1-dodecanol as a co-solvent could resolve this issue because 1-dodecanol might act as a partial capping agent for the highly reactive W-Cl functionality in WOCl₄. To investigate the capping effect of 1-dodecanol on WOCl₄, we carried out the synthesis of WₓVO₂ by varying the molar mixing ratio of EG to 1-dodecanol at 1:0.5, 1:1, and 1:2 at fixed amounts of NH₄VO₃ to WOCl₄ at 10 and 0.277 mmol, respectively. Figure 1a shows the XRD patterns of WₓVO₂ prepared from the 1:1 mixture of EG to 1-dodecanol has the lowest MIT temperature, although the fixed amount of WOCl₄ could be readily combined with EG via an exothermic reaction between WOCl₄ and hydroxyl groups that make byproducts of HCl. Thus, one might expect that WOCl₄ combined with EG participates in the formation of VEG, thereby resulting in the insertion of tungsten atoms into VO₂ (M) during calcination. However, when 2.77 mol% of WOCl₄ to NH₄VO₃ was added into the reaction mixture of ammonium metavanadate and EG at the 1:0 mixing ratio of EG to 1-dodecanol, the final product gained after calcination did not show a highly crystalline structure in its XRD pattern, as shown in Figure 1a. Additionally, the XRD pattern was not matched with that of VO₂ (M). This result can be ascribed to the incomplete synthesis of linear VEG via a condensation reaction between NH₄VO₃ and EG because WOCl₄ with four reactive W-Cl functionalities to EGs can interrupt the formation of the linear VEG.

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drop from 68 °C, the original MIT temperature of VO₂ (M), and indicate successful tungsten doping via the polyl method. Furthermore, it should be noted that WₓVO₂ prepared from the 1:1 mixture of EG to 1-dodecanol has the lowest MIT temperature, although the fixed amount of WOCl₄ was used for all calcinated samples.

To investigate the origination of these variations in the MIT temperatures, we measured SEM images of VEG synthesized without using 1-dodecanol and WOCl₄ as a reference and W-VEGs prepared with varying mixing ratios of EG to 1-dodecanol at the fixed WOCl₄ concentration of 2.77 mol% relative to NH₄VO₃ (Figure 2). The SEM images of VEG in Figure 2a looks like a mixture of square rods at the nano- and micrometer scales, which is similar to nanorods found in the literature [24]. This morphology reflects VEG crystals based on one dimensional chain of square pyramids sharing edges with the formula VO(OCH₂CH₂O) [19], as shown in Scheme 1. When 1-dodecanol was not used, the SEM image of W-VEG, as can be seen in Figure 2b, showed microcrystals with rod-like morphologies and a square cross section. The side length of the square cross section was around 1 µm. This morphology did not significantly deviate from that of VEG without using the tungsten precursor, as can be seen in Figure 2a.

With the addition of 1-dodecanol at 1:0.5 and 1:2, as shown in Figure 2c,e, the edges of the crystals were smeared, and the resulting morphology was a mixture of rods and smeared aggregates. The SEM image at 1:1 shown in Figure 2d shows morphologies with sharp edges, but the sizes and lengths of the microcrystals were significantly decreased in comparison to those at a 1:0 ratio of 1-dodecanol.

Figure 2. FE-SEM images of VEG (a) and W-VEGs (b–e) obtained with different mixing ratios of EG to 1-dodecanol at (a) 1:0 without using WOCl₄, (b) 1:0, (c) 1:0.5, (d) 1:1, and (e) 1:2 at a fixed WOCl₄ concentration of 2.77 mol% relative to NH₄VO₃, respectively. (scale bar = 1 µm).

One hypothesis to explain the variation in the morphologies of W-VEG microcrystals is that WOCl₄ reacted with 1-dodecanol, which significantly influenced the crystal morphologies. The reaction between NH₄VO₃ and EG is like the oligomerization of two monomers, resulting in VEG with a one-dimensional chain of VO₃ square pyramids, as shown in Scheme 1 and the literature [18]. Our results suggest that the WOCl₄ combined with 1-dodecanol might interrupt the growth of VEG in one dimension, resulting in the decrease in tungsten doping after calcination of the W-VEG, and when at the 1:1 molar mixing ratio, such an interruption might be alleviated. In the mixture of EG and 1-dodecanol, WOCl₄ can form many different chemical structures shown in Scheme 2. Without using 1-dodecanol, species I, II, and III are primarily formed, and species I might hinder the formation of the
one-dimensional chain of the VO₅ square pyramids due to its multiple functionalities. Species IV, V, VI, and VII, which can be produced by the reaction of WOCl₄ with both of EG and 1-dodecanol, should also significantly influence the final morphologies of W-VEGs. In particular, species V might be the main product of the reaction between WOCl₄ and the mixture of EG and 1-dodecanol at a 1:1 ratio due to the statistically equal opportunity for the reaction, which occurs only if the reactivities of WOCl₄ to EG and 1-dodecanol are identical; this in turn can be responsible for the improved tungsten doping.

To further investigate the credibility of our hypothesis and speculations and the effects of the addition of 1-dodecanol, we examined the FT-IR spectra of W-VEGs prepared at different mixing ratios of EG and 1-dodecanol. The FT-IR spectra of W-VEGs shown in Figure 3a in a range of 4000 to 400 cm⁻¹ clearly present IR bands of O-H stretching (~3450 cm⁻¹), C-H stretching (3000 to 2800 cm⁻¹), O-H/C-H bending (1800 to 1500 cm⁻¹), C-O stretching (1239.2 cm⁻¹), V = O/W = O stretching (1100 to 950 cm⁻¹), and V-O/W-O stretching (700 to 400 cm⁻¹). We found that the FT-IR spectrum of W-VEG prepared at the 1:1 mixing ratio of EG to 1-dodecanol was distinctly different from those of other W-VEGs. When we observed the C-H stretching bands in the range of 3000 to 2800 cm⁻¹, the peak positions of W-VEGs prepared at 1:1 were around 2958.6, 2925.8, and 2853.5 cm⁻¹ while those at 1:0, 1:0.5, and 1:2 appeared at around 2958.6, 2940.3, and 2879.5 cm⁻¹, as shown in Figure 3b. The IR bands that appeared in the range of 1800 to 1500 cm⁻¹ are ascribed to the overlapping spectra of O-H bending (~1670–1620 cm⁻¹) and C-H bending in the EG units (~1598 cm⁻¹) [25–27]. In Figure 3c, a shoulder peak in the range of 1790 to 1700 cm⁻¹ appeared for W-VEG at the 1:1 mixing ratio, while only a strong band centered at around 1638 cm⁻¹ was shown for all the other W-VEGs at the 1:0, 1:0.5, and 1:2 ratios. In addition, a strong IR band characteristic for C-O stretching appeared at 1239.2 cm⁻¹ and a shoulder appeared at around 1286 cm⁻¹ in the FT-IR spectrum of W-VEG at the 1:1 ratio. In contrast, two independent peaks at 1253.6 and 1231.5 cm⁻¹ appeared in the FT-IR spectra of W-VEGs at the 1:0, 1:0.5, and 1:2 ratios. All these variations in the FT-IR spectrum of W-VEG at the 1:1 ratio strongly suggest that the dodecyloxy moiety combined with WOCl₄ was incorporated into the W-VEG structure, thereby distinctly changing the peak positions of C-H stretching, O-H/C-H bending, and C-O stretching. One of the most plausible mechanisms to explain these results can be the reaction of NH₄VO₃ and EG with WOCl₄ combined with both EG and 1-dodecanol to form W-VEG.

Scheme 2. Chemical structures of species that can be formed via reactions of WOCl₄ with a mixture of EG and 1-dodecanol at different mixing ratios.
Figure 3. (a) FT-IR spectra of W-VEGs obtained with different mixing ratios of EG to 1-dodecanol at ratios of 1:0, 1:0.5, 1:1, and 1:2 at a fixed WOCl4 concentration of 2.77 mol% relative to NH4VO3, and enlarged spectra of (b) C-H stretching, (c) O-H/C-H bending and (d) C-O stretching.

Then, we investigated the effects of the amount of tungsten precursor on the changes in the MIT temperature of WxVO2. We fixed the molar mixing ratio of EG to 1-dodecanol at 1:1 for further investigation. At the fixed conditions of NH4VO3, EG, and 1-dodecanol, the increasing concentrations of WOCl4 were used for the synthesis of WxVO2. All XRD patterns of WxVO2 synthesized at 0, 2.77, 5.53, and 11.08 mol% of WOCl4 to NH4VO3 in Figure 4a show that the VO2 (M) phase (JCPDS No. 43-1051) was successfully synthesized, although there exists a portion of the V6O13 phase with the addition of WOCl4. With the further addition of WOCl4 beyond 11.08 mol%, only V6O13 was synthesized (data not shown), indicating the oxidation of VO2 (M) due to the excessive addition of WOCl4. The MIT temperatures decreased from 68.07, 61.23, and 56.95 down to 51.12 °C at WOCl4 concentrations of 0, 2.77, 5.53, and 11.08 mol%, respectively, clearly showing the effects of tungsten doping (Figure 4b). This decrease in the MIT temperature is ascribed to the formation of the rutile phase VO2 (R) with the W doping, as indicated in literature [28]. The enhancement of (110) peak at 2θ = 26.8° is characteristic for the VO2 (R) phase [28], and clearly shown in the XRD patterns of WxVO2, supporting this mechanism. It should also be noted that the full width at half maximum (FWHM) of the melting transitions in the DSC thermograms (Figure 4b) drastically increased with the addition of WOCl4 from 3.9, 4.4, 6.2, to 11.4 °C. These results show that the crystallinity of WxVO2 was significantly decreased with increasing concentrations of WOCl4. Furthermore, the intensity of the melting peak drastically decreased with the increasing W doping, indicating that the activation energy for the MIT was reduced. In the monoclinic VO2 structure, V-V intervals are alternative (2.65 and 3.12 Å) while those in the rutile VO2 above the MIT are symmetric (2.87 Å). When V atoms are partially substituted with W atoms, the V-V intervals are shrunk, decreasing the structural differences between the monoclinic and rutile structure, and thereby reducing the activation energy [29]. The amounts of tungsten doped to vanadium in WxVO2 (M) were 0.33, 0.97, and 2.07 mol%, as determined by ICP-AES.
measurements (Table 1). These figures represent significantly decreased amounts in comparison to
the tungsten precursor WOCl$_4$. Hereafter, the calcinated W$_x$VO$_2$ from W-VEGs prepared at WOCl$_4$
concentrations of 0, 2.77, 5.53, and 11.08 mol% are denoted by W$_{0.0033}$VO$_2$, W$_{0.0097}$VO$_2$, and W$_{0.0207}$VO$_2$,
respectively. Our results showed that only 10~20% of tungsten added into the reaction mixtures was
incorporated into the final W$_x$VO$_2$ compounds and indicate that a significant portion of WOCl$_4$ that
reacted with EG and 1-dodecanol did not participate in the formation of W-VEGs. We presumed that
many of the species shown in Scheme 2 might not be appropriate for the formation of W-VEGs.

| W in Reaction Mixtures (mol%) | W in W$_x$VO$_2$ (mol%) |
|------------------------------|-------------------------|
| 2.77                         | 0.33                    |
| 5.53                         | 0.97                    |
| 11.08                        | 2.07                    |

To examine the origination of these broadening melting peaks resulting from an increase in the
WOCl$_4$, we analyzed W-VEGs by measuring SEM images. Figure 5a shows that the VEG synthesized
at the 1:1 mixing ratio of EG to 1-dodecanol without adding the WOCl$_4$. The VEG has a nanowire
morphology with a square or rectangular cross section. The nanowire morphology with a high
aspect ratio over 10 is clearly different from that of VEG with a nanorod or microrod morphology
prepared without using 1-dodecanol, which can be observed in Figure 2a. These results demonstrate that
1-dodecanol acts as a capping agent to block a specific crystal plane, thereby enhancing one-dimensional
growth when VEG is synthesized. With the addition of WOCl$_4$, the nanowire morphology disappears,
presenting irregular crystal morphologies, as shown in Figure 5b–d. The crystal sizes of W-VEGs
decreased from the micrometer-scale at 2.77 mol% to the nanometer-scale at 5.53 and 11.08 mol%
of WOCl$_4$, as shown in Figure 5b–d, respectively. We ascribe this disappearance of the nanowire
morphology and the decrease in the crystal sizes to the increasing portion of dodecyloxy moieties in
W-VEGs. When the bulky alkyl side chains are incorporated into the crystal structure of W-VEGs,
they might act as defects to the formation of the one-dimensional chain-like structures shown in
Scheme 1 and the crystallization of the chains.
These results indicate that the WxVO2 compounds prepared via our modified polyol method utilizing 1-dodecanol present distinct thermochromic properties. We measured the transmittance spectra of the VO2 and W0.0207VO2 crystals dispersed in ethanol at 20 and 70 °C as two representatives. When the UV-Vis-NIR curves of 20 and 70°C were compared, there were no significant changes in the range of visible light shorter than 780 nm. However, in the NIR region, we observed that the transmittances of ethanol dispersions of VO2 and W0.0207VO2 at 70 °C were significantly decreased from those at 20 °C. The solar modulation Tsol at each temperature was calculated by Equation (1), where $\phi(\lambda)$ and $T(\lambda)$ are the solar irradiation spectrum for an air mass of 1.5 (corresponding to the sun standing 37° above the horizontal) [30] and transmittance at specific wavelengths $\lambda$, respectively, and $\Delta T_{sol}$ was estimated by Equation (2) [9]. The luminous transmittance was also calculated by Equation (3) where $\phi_{lum}(\lambda)$ is the spectral sensitivity of the light-adapted eye [18]. The estimated $\Delta T_{sol}$ of VO2 without tungsten doping was 2.5% and that of W0.0207VO2 was 21.8%. The usefulness of our modified polyol method utilizing WOCl4 and 1-dodecanol to prepare tungsten-doped VO2 is evidenced by the significantly enhanced solar modulation of the ethanol dispersion of W0.0207VO2 with the manifestation of the tungsten doping. The luminous transmittance of W0.0207VO2 at 20 °C estimated by Equation (3) was 66.8% while that of VO2 was 78.2%. This decrease in the luminous transmittance with the tungsten doping can be ascribed to serious light scattering of W0.0207VO2 in comparison to VO2. Sizes of VO2 and W0.0207VO2 nanoparticles estimated by analyzing their SEM images shown in Figure 6c,d are 156 ± 81 and 287 ± 84 nm, respectively. These results indicate that the W0.0207VO2 nanoparticles with bigger sizes than the VO2 nanoparticles significantly scatter light, resulting in the decrease in transmittance. It should be noted that the average crystallite sizes of VO2 and V6O13 estimated by using XRD patterns in Figure 4a and the Scherrer equation [31] are 63.8 and 36.2 nm, respectively. The bigger size of the W0.0207VO2 nanoparticles than their crystallite sizes indicate that the nanoparticles have polycrystalline textures. On the other hand, the thermochromic properties gained in our study are compared with those of WxVO2 with the MIT temperature ($T_c$) in a range of 40–45 °C in Table 2. The $T_{lum}$ at 20 °C and $\Delta T_{sol}$ of W0.0207VO2 in this study are higher than those of reported materials except the $T_{lum}$ at 20 °C of the W-doped...
VO\textsubscript{2}/polyvinylpyrrolidone coating as presented in the Table 2 [32–35]. This comparison suggests that W\textsubscript{x}VO\textsubscript{2} materials in our study have a great potential for thermochromic applications.

\[
T_{\text{sol}} = \frac{\int \varphi(\lambda) \cdot Tr(\lambda) \cdot d\lambda}{\int \varphi(\lambda) \cdot d\lambda}
\]

\[
\Delta T_{\text{sol}} = T_{\text{sol}}(20^\circ \text{C}) - T_{\text{sol}}(70^\circ \text{C})
\]

\[
T_{\text{lum}} = \frac{\int \varphi_{\text{lum}}(\lambda) \cdot Tr(\lambda) \cdot d\lambda}{\int \varphi_{\text{lum}}(\lambda) \cdot d\lambda}
\]

Figure 6. Transmittance spectra of ethanol dispersions of (a) VO\textsubscript{2} and (b) W\textsubscript{0.0207}VO\textsubscript{2}, and SEM images of (c) VO\textsubscript{2} and (d) W\textsubscript{0.0207}VO\textsubscript{2} nanoparticles.

Table 2. A summary of thermochromic properties of tungsten-doped VO\textsubscript{2}.

| Samples          | W in W\textsubscript{x}VO\textsubscript{2} (%) | T\textsubscript{c} (°C) | T\textsubscript{lum} at 20 °C (%) | \(\Delta T_{\text{sol}}\) (%) | Ref. |
|------------------|-----------------------------------------------|------------------------|----------------------------------|-------------------------------|-----|
| Mesoporous film  | 0.4                                           | 43.0                   | 61.6                             | 11.4                          | [31]|
| Coating with PVP | 3                                             | 44.4                   | 68.3                             | 20.4                          | [32]|
| Core@SiO\textsubscript{2} shell | 2                                           | 43.0                   | 39.1                             | 12.9                          | [33]|
| NP Film          | 0.7                                           | 42.7                   | 63.4                             | 11.7                          | [34]|
| Dispersion       | 2.07                                          | 51.1                   | 66.8                             | 21.8                          | This study |
4. Conclusions

In this study, we carried out the synthesis of tungsten-doped VO$_2$ via a polyol method based on ammonium metavanadate and EG by utilizing WOCl$_4$ and 1-dodecanol as the tungsten source and capping agent, respectively. By conducting extensive characterizations using XRD, DSC, SEM, FT-IR, UV-Vis-NIR spectroscopy, and ICP-AES analysis, it was suggested that WOCl$_4$ coupled with both EG and 1-dodecanol at an optimal ratio was responsible for the successful incorporation of tungsten into W-VEG in the creation of the calcinated compound, W$_x$VO$_2$. Other popular tungsten sources such as WCl$_6$ and Na$_2$WO$_4$ were not effective for the tungsten doping in the polyol process, which indicates the usefulness of our modified polyol method that utilizes 1-dodecanol and WOCl$_4$. However, it should be noted that the incorporation of bulky dodecyl chains into W-VEG seems to result in an increased FWHM value for the melting transition and that the current MIT temperature of W$_x$VO$_2$ at around 51 °C should be further decreased to near room temperature for practical thermochromic applications. In addition, the decrease in the luminous transmittance with the tungsten doping should be improved. These issues suggest that further investigations should be undertaken to find alcohol capping agents less bulky than 1-dodecanol and processes to avoid aggregations.

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