NEAR INFRARED CUT-OFF OF COMPOSITE FILM WITH VARIOUS PEROVSKITE OXIDE BASED NANOPARTICLES

Jae Young Kim, Hyun Jin Yoon, Eun kyoung kim, Seung Yong Jeong, Sangkug Lee, Gyo jic Shin and Kyung Ho Choi

Center for Green Materials Technology, Korea Institute of Industrial Technology, 35-3, Hongcheon-ri, Ipjang-myeon, Seobukgu, Cheonan-si, Chungnam-do 330-825, Republic of Korea

soo@kitech.re.kr, hj_yoon@kitech.re.kr, imkek@kitech.re.kr, jsy2837@kitech.re.kr, skdlee@kitech.re.kr, gyshin@kitech.re.kr, khchoi@kitech.re.kr

Abstract

Homogenous cesium tungsten tri-oxide (Cs$_3$W$_1$O$_3$) and powder was prepared by solvothermal reaction using (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$ and Cs$_2$CO$_3$ aqueous solution followed by annealing. The cesium doped tungsten tri-oxide (Cs$_3$W$_1$O$_3$) nanocomposite films was deposited by the sol-gel bar-coating method onto PET-film (polyethylene terephthalate film, thickness 186 μm) substrate. The structure and sizes of ceramic particles was observed XRD and PSA spectrometer, the optical properties of their films were investigated by UV-VIS, NIR spectrometer. Synthesized particles typically formed cubic structure for good absorption of NIR, size observed as being 30-100 nm and <150 nm. Cs$_3$W$_1$O$_3$ nanoparticles showed a high transmittance in the visible wavelength region as well as excellent shielding capability of near-infrared (NIR) wavelength, indicating that Cs$_3$W$_1$O$_3$ nanoparticles have the appropriate characteristic as solar filter application.

Keywords: Thermal insulating materials(TIM), Perovskite, Nanocomposite film, Nanodispersion, Near-infrared (NIR) shielding.

1. INTRODUCTION

Recently, many kinds of ceramic particles with various size extensively have been attracted the very much interest for UV-visible and Near-infrared (NIR) region cut-off behavior. Particularly, tin-doped indium oxide (ITO) and antimony-doped tin oxide (ATO) widely have used as material to perform purpose of NIR-shielding effect. At this point, WO$_3$ exhibits the transparent property in the UV-visible, NIR lights and has a wide band gap of 2.62 eV. Moreover, WO$_3$-based electrochromic devices are almost being examined for smart film applications with changeable modulations in optical spectra. A metallic conductivity and strong NIR absorption can be induced when free electrons are introduced into crystals by either decreasing the oxygen content or by adding ternary elements. The oxygen deficiency in tungsten oxides leads to a complex-ordered structure known as the Magneli structure, while the ternary addition of the positive ions leads to the tungsten bronze structure. It has been reported that the tungsten bronzes with the hexagonal phase are of particular interest in the application of electrochromic devices owing to the relatively high diffusion coefficients of hydrogen ions and metal ions compared with those of the orthorhombic phase and WO$_3$. Until now, study on the synthesizing WO$_3$ with different morphologies and properties has been widely reported [1-3]. However, there is limited work reported on the synthesis and characterization of only Cs$_3$WO$_3$ nanorod with controlled morphology by solvothermal reaction [4-6]. Furthermore, heat-shielding properties of Cs$_3$WO$_3$ nanoparticle have not been reported.

In this study, the four kinds of perovskite-based (Cs$_3$W$_1$O$_3$) composite films were prepared by mixing Urethane acrylic/UV-coating binder and the properties of UV-visible and NIR absorption spectra of their films were investigated by UV-visible, NIR and PSA spectrometer.
2. EXPERIMENTALS

The synthesis of series is summarized outlined in Scheme 1.

<table>
<thead>
<tr>
<th>A-site (Cs)</th>
<th>Ammonium molybdate</th>
<th>Heating temp / time</th>
<th>Annealing temp / time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33 mol</td>
<td>1 mol</td>
<td>550°C / 1h</td>
</tr>
<tr>
<td>2</td>
<td>0.50 mol</td>
<td>1 mol</td>
<td>550°C / 1h</td>
</tr>
<tr>
<td>3</td>
<td>0.75 mol</td>
<td>1 mol</td>
<td>550°C / 1h</td>
</tr>
<tr>
<td>4</td>
<td>1.00 mol</td>
<td>1 mol</td>
<td>550°C / 1h</td>
</tr>
</tbody>
</table>

Scheme 1. Synthetic routes for the nanoparticles.

Synthesizing of homogenous Cs₅W₃O₁₉ powder and Cs₂CO₃ of various concentration were mixed in aqueous, dried at 180 °C for 8 hr. The precursor as dried at 180 °C was heated in a tubular furnace at 450 °C for 1 hr with H₂/N₂ gas flow at H₂/N₂=90/10, followed by annealing at 800 °C in an N₂ gas for 0.5 hr. As for cesium tungsten oxide powders, Cs₅W₁O₃, cesium content at A = 0.33, 0.50, 0.75 and 1.00 mol were synthesized this study. The as-produced powders were dispersed by turbomill with iron ball for 2hr and the zirconia bead for 1 hr respectively. In the other hand, nanocomposite films were prepared with mixing urethane acrylic/UV coating binder and well dispersed persvokies sol by using bar coater. Dispersion and coating binder were mixed well in vial with rotating mixer. The prepared films were dried at 80 °C for 1min in heating chamber and illuminated with the mercury UV lamp UV-curing equipment at intensity 800 W/cm for 20 sec. The Coated composite film thickness was measured with cross section of each film using scanning electron microscope (SEM, JSM6700F, JEOL). The optical properties were evaluated with UV-VIS spectrophotometer (model UV-2550, SHIMADZU, Japan) range of 200~800 nm and FT-IR/FT-NIR spectrometer (model spectrum 400, PerkinElmer, USA) range of 800~2,000 nm.

3. RESULTS AND DISCUSSION

The hexagonal structure of the CsW₁O₃ powder was confirmed both by Scanning electron microscope (SEM) and by X-ray diffraction (XRD). A synthesis of CsₓW₁O₃ particle with annealing temperature of 800°C was morphology as measured by SEM. The CsW₁O₃ particles under the 100 nm can be observed in Fig. 1. Each CsW₁O₃ nano-particle was aggregated with the mass of the few micron size. Those clusters shatter to pieces by pulverization dispersed methods.

Fig. 1. Scanning electron microscope (SEM) image of Cs₀.₃₃W₃O₁₉ nanoparticle.
The typical XRD pattern of synthetic Cs$_{0.33}$W$_1$O$_3$ nano-particle with the 800 °C annealing temperature sample was presented in Fig. 2. The particle shows perovskite tungsten bronze of hexagonal symmetry as the major phase along with 2-3 weak lines WO$_3$ of cubic symmetry. The peaks could be indexed to the hexagonal cesium tungsten bronze (JCPDS No. 831334). This result indicated that the nanoparticles obtained by annealing at 800 °C prefers the hexagonal tungsten bronze structure. It was well known that the relatively larger ions such as Ti (0.150 nm), Rb (0.152 nm), and Cs (0.170 nm) compared with Li, Na etc. could fit better in the hexagonal vacant tunnels (0.163 nm) in the hexagonal tungsten bronze structure rather than in the rectangular vacant tunnels in the cubic tungsten bronze structure. In the other hand, this result suggested that the typical hexagonal structure of Cs$_{0.33}$WO$_3$ with remarkable absorption of NIR was formed by annealing at 800 °C.

Fig. 2. Effect of annealing temperature to Cs$_{0.33}$W$_1$O$_3$; XRD (X-ray diffraction, 2 °/min ; 5 90 °) ; annealing at 800 °C.

Fig. 3 represented the relation between NIR shielding effect and Cs$_{x}$W$_1$O$_3$ concentrations. According to the illustration, as the Cs$_{x}$W$_1$O$_3$ concentrations increased from 0.5, 1.0, 1.5, and 2.5 wt%, NIR transmittance value commonly were declined whereas NIR transmittance increased with increasing ‘A’ values of Cs$_{x}$W$_1$O$_3$. Particularly, in case of clearly indicated that the distinct absorption curve around 1,000nm. This discrepancy could be explained by an underestimation of short-range order effects in the XRD pattern whereas in phonon absorption short-range-order effects are seen mainly. Single-phase hexagonal structure sample (A=0.33) only possess a clear increase in absorption that increases with increasing contents.

We were coated by bar-coating methods onto the PET substrate with few micron and ≤100nm size of perovskite oxide. Those composite films were measured by UV/VIS, NIR spectrometer. As well known, visible light transmittance can be made high as the particles size is much smaller than the visible wavelength. The composite film of coated with few micron size particles was scattering for the most part of visible light region [7-9].
Because the perovskites-based nanomaterials exhibit strong absorption of NIR wavelength, it is expected to convert the absorbed radiation to local heat directly to photothermal conversion properties of the nanomaterials, the prepared composite film were put on a paper and then irradiated by a 250 W IR lamp for 30 s. The temperature distribution was recorded by thermographic analysis. Fig. 4 shows the image of Cs$_{0.33}$WO$_3$ composite film. The measurement was performed at an ambient temperature of 25 °C. Within only 20 s, the temperature of the composite film increased from 25 to 135 °C, whereas the temperature of the other around the composite film did not rise very much, indicating the quick conversion of absorbed NIR wavelength energy to local heating energy on the composite film.

Fig. 4. Thermographic images of the Cs$_{0.33}$WO$_3$ 2.5 wt% nanocomposite film (irradiation by a 250 W IR lamp).

4. CONCLUSION

In this work, the ceramic nano-composite films with homogeneous dispersions of tungsten bronze nanoparticles with ternary additive cesium have been prepared by mixing urethane acrylic/UV-coating binder and dispersed sol depending on the dispersed time and the particle contents. Furthermore, we are synthesized the Cs$_{x}$W$_1$O$_3$ with controlling contents and the using annealing at 800 °C in an N$_2$ gas for 1h respectively. The structure and sizes of ceramic particles was observed XRD and PSA spectrometer, the optical properties of their films were investigated by UV/VIS, NIR spectrometer. Synthesized particles typically formed hexagonal structure for good absorption of NIR, size observed as being 30~100 nm and ≤ 150 nm. Especially, remarkable absorption of NIR wavelength ranges makes ceramic composite films good candidate for use as a heat shielding window, it clearly shows useful for applications where heat shield is required.
REFERENCE