Aerosol-assisted Production of NIR Shielding Nanoparticles: Sodium Tungsten Bronze

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ABSTRACT

An aerosol-assisted process for continuously producing sodium tungsten bronze particles in one step was proposed. The effects of the precursor solution, solvent, heating temperature, and moisture concentration on the quality (i.e., crystallinity) of the products were systematically investigated. The mechanisms for the particle formation and the chemical reactions involved in this process were also studied. By varying the atomic ratio of sodium to tungsten in the precursor solution, sodium tungsten bronze particles in the cubic ($\text{Na}_{0.70}\text{WO}_3$) and tetragonal ($\text{Na}_{0.57}\text{WO}_3$) phases were monophasically produced. Particles in both phases showed near infrared (NIR) shielding properties. However, cubic-phase particles ($\text{Na}_{0.70}\text{WO}_3$) possessed higher visibility in the visible light range due to their lower impurity content and higher crystallinity.

Keywords: NIR shielding particles; Sodium tungsten bronze crystal; Aerosol-assisted synthesis.

INTRODUCTION

Near infrared (NIR) light is the radiation that has the wavelength ranging from 0.75 μm to 1.5 μm , which makes ~18% solar radiation energy on the surface of the earth according to the previous measurement (ASTM International, 2012). The thermal effect of NIR increases the energy consumption for air conditioning (AC) of a building/automobile in hot weather. In cold weather, keeping NIR from escaping to the outside can also reduce the loss of thermal energy by radiation. The energy uses for heating, ventilating and air conditioning (HVAC) of buildings is estimated at ~50% of the total energy consumption for the building service in the U.S. and UK (Pérez-Lombard *et al.*, 2008). The energy for HVAC operation of automobiles is ~17% (Lambert and Jones, 2006). Shielding the NIR light through the windows of buildings and automobiles is thus in great demand for the energy-saving.

Various functional materials could be utilized to shield NIR from penetrating through transparent media such as glass. The commercial NIR shielding glass coating includes dielectric-Ag-dielectric films, metal-free solar reflecting films and functional particles-imbedded film (Padiyath *et al.*, 2007). The dielectric-Ag-dielectric film reflects the NIR by the multiple-film structure of Ag layers and dielectric oxide layers, e.g., indium tin oxide (ITO) and antimony tin oxide (ATO) (Schaefer *et al.*, 1997). Ag is applied in the layer

because of its unique optical properties (Berning and Turner, 1957; Berning, 1983). Both ITO and Ag are expensive due to their production scale and storage (Padiyath *et al.*, 2007). In addition, the manufacture of dielectric-Ag-dielectric films is by the sputtering processing, in which highly precise thickness control of the Ag layer is required, since the extra thickness of Ag layer would result in the dramatic reduction of visible light transmission (Padiyath *et al.*, 2007). Furthermore, the presence of Ag layer could reduce the signal strength of cell phone, GPS etc. due to its high electrical conductivity. For the metal-free solar reflecting films, their NIR shielding function relies on the refractive index difference of polymer layers (Weber *et al.*, 2000). The above films typically have laminated construction with hundreds of layers, and the commercial products of the above films have been applied on automobile since early 2000s (Padiyath *et al.*, 2007). However, the irreversible aging of polymer-based films is typically occurred because of the C–C bond is vulnerable to the high-energy UV photons in solar light. In general, the lifespan of a piece of high-quality metal-free solar reflecting film is ~10 years (Tintcenter.com, 2011). The above makes the metal-free films unpopular in the permanent cases such as architectural windows.

Without the requirement of any special film structure, the other candidates for the NIR shielding are the functional-particle-imbedded films. Examples of these functional particles are rare-earth hexaboride (ReB_6 , Re = La, Ce, Pr, Nd and Gd) and tungsten bronze (M_xWO_3 , M = Li, Na, Cs, Ru, K, NH_4 etc.) in the previous studies (Kimura *et al.*, 1990; Takeda *et al.*, 2008; Adachi *et al.*, 2010; Guo *et al.*, 2010, 2011, 2012a). The performance of rare-earth hexaboride particles is related with the particle size because the NIR

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absorption is based on the localized surface plasma resonance (LSPR) of conduction electrons (Takeda *et al.*, 2008). Particles in a certain size range exhibits the effective NIR shielding. The range of wavelength for shielding NIR is also selective for the above particles (Kimura *et al.*, 1990; Takeda *et al.*, 2008). Different from the LSPR mechanism, tungsten bronze particles shield the NIR via the insertion of alkali ion into tungsten oxide crystal lattice to form a solid solution, which is commonly observed in either the cubic or tetragonal crystal phase. Due to the ternary addition of positive ions, free electrons are induced to interact with photons by dipole absorption, which is the reason for general wide-range NIR absorption by tungsten bronze (Svensson and Granqvist, 1984; Takeda and Adachi, 2007). Furthermore, as a family member of tungsten trioxide, tungsten bronze is insoluble in water and all acids except hydrofluoric acid (Luo, 2010). It implies that tungsten bronze is chemically stable in the indoor/outdoor environments.

The initial synthesis of tungsten bronze was reported by Wöhler (1824) via the thermal reduction of fused salts. Various tungsten bronzes (M_xWO_3 , $M = \text{Li, Na, K, Ru, Cs}$) were later produced by the thermal reduction method (Straumanis, 1949; Straumanis and Hsu, 1950; Magnéli and Blomberg, 1951). Combined with electrolysis, the high-quality crystal (in millimeter sizes) of tungsten bronzes with the tuned x in M_xWO_3 were produced (Brown and Banks, 1954; Shanks, 1972). The melt salt reaction generally requires to be in high temperatures and typically results in macro-sized bulk products (~3 cm). However, for the coating applications, micro- or nano-particles are more friendly to the processing (compared with macro-sized products). Grinding large crystals into the powder form is expensive in energy and easily contaminated. The wet chemical method has thus been used to first prepare the sol-gel precursor composed by amorphous tungsten oxide, and then to obtain the tungsten bronze powder through the thermal hydrogen reduction ($M_{0.33}WO_3$, $M = \text{Ti, Rb, Cs}$) (Takeda and Adachi, 2007). By the time-consuming solvothermal reaction, nanoparticle of tungsten bronzes (M_xWO_3 , $M = \text{K, Ru, Cs, NH}_4$) were directly synthesized at low temperature (Guo *et al.*, 2010, 2011, 2012a, b). Although multiple methods were proposed to produce tungsten bronze particles, the worldwide production of tungsten bronze powders remains extremely low. It is because the processing methods including the melting salt, powder grinding, hydrothermal and calcination is energy-costly and time-consuming.

Aerosol-based processing has been applied to produce particles in the sub-micrometer and even nanometer size range (Messing *et al.*, 1993; Eerikainen *et al.*, 2003). Because of its continuous operation at high rate (Charitidis *et al.*, 2014) and the high reproducibility for the product quality and purity (Gurav *et al.*, 1993), aerosol-based process is in general considered as a synthesis method easy for the future scale-up production. Furthermore, the characteristics of particles could be controlled in tube reactors by varying the tube temperature, flow rate and chemical composition of solutions in aerosol-based synthesis (Gurav *et al.*, 1993). To make the synthesis of tungsten bronze easy for the future scale-up production, the flame-assisted method was proposed

in the work of Hirano *et al.* (2018) for producing cesium tungsten bronze particles. In their report, the precursor can be continuously produced by flame-assisted synthesis. However, another individual annealing remains necessary to promote the crystallinity and eliminate the multiple phases. Furthermore, cesium is used as doping ion into the tungsten oxide in their work. Since the nature abundance of cesium is very low, the price of cesium compound is very high for large-scale producing of NIR shielding materials. So, in order to make the tungsten oxide bronze to be feasible for industry-scale producing for NIR shielding, a simple one-step method which can continuously produce crystallized and monophasic particles remains a challenge. The needs are also found in electrochromic and gas-sensing nanomaterial, which rely on the crystalline tungsten oxide compounds.

In this work, we used a droplet-based process to efficiently synthesize sodium tungsten bronze particles in crystalline and single phase. By varying the composition of precursor solutions, the effect of particle crystal phase on the optical property was investigated. The near-infrared absorption property of as-synthesized sodium tungsten bronze nanoparticles in cubic and tetragonal phases were evaluated.

METHODS AND EXPERIMENTAL SETUP

Fig. 1 shows the schematic diagram of the experimental setup for preparing sodium tungsten nanoparticles. The system utilized a custom-made Collision atomizer to generate the polydisperse droplets from the precursor solutions. Different from a typical Collision atomizer in which the spray solution is kept in the spray chamber, the spray solution (#0) is fed to the spray nozzle of this atomizer from a syringe driven by a syringe pump (NE-1000; New Era Pump Systems). The compressed N_2 gas was used as the spray and carry flow to operate the atomizer. The pumping rate was set at $300 \mu\text{L min}^{-1}$. The pressure of nitrogen carry gas flow was set at 25 psi, resulting in the flow rate of $\sim 2 \text{ L min}^{-1}$ (standard liters per minute).

The #0 solution is the mixture of two solutions, A and B, in different percentages by volume. Solution A was prepared by dissolving the 7.93 g (0.02 mol) of tungsten chloride (WCl_6 ; Acros Organics) and the 1.16 g (0.02 mol) of sodium chloride ($NaCl$; Acros Organics) in 1000 mL methanol (CH_3OH ; Alfa Aesar). The above solution was sealed in a bottle for continuously stirring for 3 days (at the room temperature). Solution B was prepared in the same process as described without the addition of sodium chloride. All these solutions were kept sealed in glass bottles and stored in chemical closets at room temperature. The molar Na/W ratio of the test #0 solution is summarized in Table 1. The #0 solution was transferred to a syringe for the experiments.

Prior to entering the high-temperature tube furnace, the produced droplet stream in the atomizer was mixed with two other nitrogen flows (#1 and #2) while keeping the total flow rate of #1 and #2 at $500 \text{ cm}^3 \text{ min}^{-1}$ (standard cubic centimeters per minute). The #2 nitrogen flow bubbled through DI water kept in a container to carry water vapor. The DI water container was kept at 55°C . At the temperature, the moisture concentration in the #2 flow is 0.23 g L^{-1} . The moisture concentration was measured by weighing the water mass

Fig. 1. Schematic diagram of the experimental setup for the production of sodium tungsten bronze nanoparticles.

Table 1. The summary of Na/W ratio in the precursor solution (#0 in Fig. 1) used in this study.

Na/W atomic ratio in #0 solution	1.0	0.8	0.6	0.5	0.4	0.3	0.2	0
Solution A (vol%)	100	80	60	50	40	30	20	0
Solution B (vol%)	0	20	40	50	60	70	80	100

loss in DI water container in a specific time (1 hour). We assumed that the amount of water loss contributes to the moisture concentration in the flow. The specific moisture concentration in the total flow under different #1 and #2 flow rates were given in Table 2 for the reference. All the nitrogen flow rates were controlled by the mass flow controllers (Alicat Scientific).

The mixed flow in the total rate of 2.5 L min^{-1} was then directed into a quartz tube placed in a high-temperature tube furnace (Lindberg 1200C; Thermo Scientific). The retention time for the particle stream in the furnace was estimated at $\sim 10 \text{ s}$. The furnace setting temperature was varied from 350 to 800°C . The as-produced particles were collected on a filter medium (glass fiber filter; Pall Corporation) placed in a filter holder installed at the exit of the tube furnace. The collection flow rate was set at 2.5 L min^{-1} via a critical orifice and a vacuum pump. An additional opening line was also included in the setup to ensure the inlet of filter holder was near the ambient pressure.

To characterize sample particles, the XRD patterns of the particles were measured by X'Pert PRO PANalytical. The images and EDX spectrum of the samples were taken by the Hitachi SU-70 FE-SEM. We placed a piece of glass slide at the exit of the reactor tube in parallel with the flow direction to collect as-produced particles for SEM imaging. The XPS spectrum was analyzed by the PHI VersaProbe III scanning XPS microprobe. The UV-Visible-NIR spectrum was measured by the M-2000 ellipsometer (J.A. Woollam). The particles are dispersed in collodion/IPA (5 wt%) solution. The concentrations of particles are adjusted to maintain the transmittance at NIR range equal to each other. Then 5 mL solution is spread onto $2'' \times 2''$ glass slide to form homogeneous film. The size distribution of particles was measured with the Scanning Mobility Particle Sizer (SMPS; Model 3080 and CPC Model 3775; TSI Inc.).

Note that, when using the above setup to produce sodium tungsten bronze particles, the #0 solutions in the Na/W ratio of 1.0 to 0 were used. The #2 flow rate was kept at 0.5 L min^{-1} in the above both cases.

RESULT AND DISCUSSION

Particle Formation in the Proposed Synthesis

To understand how sodium tungsten bronze particles were transformed from droplets produced by the spray, we measured the size distributions of particles before and after the high-temperature tube furnace. In addition to the precursor solutions (i.e., with the salt concentration of only 0.02 M), methanol only, serving as both solvent and reduction agent, was used in this part of investigation. Figs. 2(a) and 2(c) shows the size distribution of particles prior to entering the tube furnace when spraying the precursor solution and pure methanol, respectively. Compared to that shown in Fig. 2(c), the size distribution shown in Fig. 2(a) has much higher number concentration and larger peak particle size. The above comparison indicates that the solvent contribution on the produced particle samples is negligible.

Figs. 2(b) and 2(d) are the size distributions of particles measured by SMPS after the high-temperature tube furnace when spray the precursor solution and pure methanol, respectively. Once passing thorough the furnace, the peak and number concentration of the particle size distribution initially produced by spray the methanol only were significantly reduced (compared with that shown in Fig. 2(c)). However, the peak and shape of the particle size distribution initially produced by spraying the precursor solution (Fig. 2(b)) remained unchanged when compared with that in Fig. 2(a) (while the number concentration was significantly reduced). The particle loss due to the diffusion and thermophoretic effect could be the reasons for the significant reduction of

Table 2. The concentration of moisture in the carry flow at different rates (tested in this study).

#1 flow rate (cm ³ min ⁻¹)	500	400	300	200	100	0
#2 flow rate (cm ³ min ⁻¹)	0	100	200	300	400	500
Moisture concn. in total flow (0.01 g L ⁻¹)	0	0.92	1.84	2.76	3.68	4.60

Fig. 2. Size distributions of particles, measured by SMPS: (a) at the entrance and (b) at the exit of tube furnace in the case of spraying the precursor solution (#0); (c) at the entrance and (d) at the exit of tube furnace in the case of spraying the methanol only.

particle number concentration. The above observation implies the scenario of resultant crystal particle formation shown in Fig. 3 (i.e., one droplet was transformed into one resultant one and the liquid solvent was nearly vaporized prior to entering the tube furnace).

Investigation of the Chemical Reaction in the Proposed Synthesis

Fig. 4 shows the EDX data of sample products obtained under the various flow rates (#2) passing through the DI water bottle. The series of EDX data evidences that the chlorine in the sample products increases from 0.28 to 5.46 wt% with the decrease of the moisture concentration (via the decrease of #2 flow rate). Based on the above finding, the entire reaction in the tube reactor could be expressed in the following Eq. (1):

In Eq. (1), the WCl_6 hydrolyzes with H_2O to form tungsten oxide in the presence of Na^+ . Since the Na^+ atom is smaller than the void in ReO_3 lattice of tungsten oxide, the sodium can easily diffuse into the lattice. According to the reaction, when there are not sufficient water molecules, the reaction would result in the additional chloride salt residue. As shown in Fig. 4, the chlorine weight percentage increases with the moisture flow rate (#2 in Fig. 1) decreases. In addition, because the methanol is strongly reductive, it reduces the tungsten from VI valence to lower ones such as V or IV, which is similar to the hydrogen thermal reduction in other previous works (Hirano *et al.*, 2018). The difference of our work compared with the previous ones is the use of methanol acting as the solvent and the reductant.

To evidence the reductive effect of methanol in the reaction, the flow rate of oxygen was added to mix with the particle flow prior to entering the tube furnace (Fig. 5). The introduction of oxygen will reduce the reductivity of the reacting flow, preventing the W(VI) from being reduced to the lower valence. Fig. 6 shows the XRD data of particle samples using the precursor solutions in different Na/W ratios in the setups (Fig. 5). It is observed that the metal state

Fig. 3. The schematic diagram of crystal particle formation in this process.

Fig. 4. EDX data of sample particle products obtained at the moisture flow rate (#2 in Fig. 1) of (a) 500, (b) 400, (c) 300, (d) 200, (e) 100, and (f) 0.0 cm³ min⁻¹. The tube furnace temperature is 800°C. The Na/W ratio is kept at 1.0.

Fig. 5. The schematic diagram of the experimental setup for verifying the reductive role of methanol used in the process.

of tungsten always presents in the sample products obtained using precursor solutions of various Na/W ratios when there is ~8% oxygen in total flow rate, and no crystal structure in the products was observed when the oxygen percentage is above or below 8%. The above finding indicates that the redox potential of methanol is not sufficient to reduce the W(VI) to the metal state (0). Alternatively, the redox

potential of intermediates might be capable. We hypothesize the intermediate is formaldehyde, whose redox potential is higher than methanol (Ferrin *et al.*, 2008). Under a certain low concentration, the oxygen partially oxidizes methanol into formaldehyde. The W(VI) could thus be reduced to the metal state by the formaldehyde. It is concluded that methanol is a good candidate for serving as the solvent and

Fig. 6. Powder-XRD data of the particle products obtained when spraying the precursor solutions with the Na/W ratio of (a) 1.00, (b) 0.80, (c) 0.60, (d) 0.40, (e) 0.20 and (f) 0.00, and under the oxygen volume ratio in total flow was 0.00, 0.04, 0.08, 0.12 and 0.16 in different color lines.

reducing agent in the studied synthesis of sodium tungsten bronze because it is able to reduce the W(VI) to W(V) or W(IV) without the over-reduction.

Effect of Precursor Solution and Furnace Temperature

To study the effect of precursor solutions on the crystal phase and crystallinity of the products, the XRD data of powder samples obtained in the cases of spraying precursor solutions (#0 in Fig. 1) in different Na/W ratios were analyzed by the simulation. The sample products under the analysis were obtained at the furnace temperature of 800°C, while the highest temperature inside furnace tube is 853°C. Fig. 7 shows the comparison of the simulated and measured

XRD data of sample products. It is found that, with the decrease of the Na/W ratio in the precursor solution, the percentage of the sample in the cubic phase is decreased and the percentage in the tetragonal phase is increased. Because of the sodium atom acting as the padding material inside the scaffold of WO_3 for supporting the structure (i.e., with sodium atoms occupying the vacancy of ReO_3 structure of WO_3), the crystal lattice tends to form in the cubic phase. In contrary, with less sodium atoms, the crystal lattice of WO_3 tends to collapse to form in the tetragonal phase. Note that, the pure WO_3 could often forms in the tetragonal phase at the room temperature (Diehl *et al.*, 1978). In specific, when the Na/W ratio in the solution is larger than 0.8, only the

Fig. 7. Comparison of the experimental and simulated patterns of powder-XRD for the sample products obtained when spraying the precursor solutions with the Na/W ratio of (a) 1.00, (b) 0.80, (c) 0.60, (d) 0.50, (e) 0.40, (f) 0.30, (g) 0.20 and (h) 0.00. The samples in (a) and (e) are cubic phase and tetragonal phase, specifically.

pure cubic phase was found in the sample products because the measured XRD patterns in Figs. 7(a) and 7(b) are well fit by the simulated ones in the cubic phase. On the other hand, when the Na/W ratio is reduced to 0.40, the sample powder is all in the tetragonal phase (Fig. 7(e)). As the Na/W ratio in the precursor solution further reduced, the crystallinity of products samples dramatically decreased and the phase composition analysis became not applicable (Figs. 7(f), 7(g) and 7(h)). The above observation is out of our expectation that crystalline tungsten oxide particles should be synthesized without the presence of sodium chloride. It suggests that the formation of crystalline Na_xWO_3 particles relies on the catalyzing by sodium ion. Since the melt point (801°C) of sodium chloride is much lower than tungsten oxide ($1,473^\circ\text{C}$), the sodium chloride acts as the ceramic flux to facilitate tungsten atoms movement and lattice conversion via the liquefaction (Daly, 1996; Eppler and Obstler, 2005). Without the sodium chloride, the amorphous tungsten oxide product requires much time to form the crystal at the same 800°C (Takeda and Adachi, 2007).

Fig. 8 shows the powder-XRD of sample products obtained at the different furnace temperature setting from 400 to 600°C (with the measured highest temperature in the tube). It is found that the furnace temperature should be set above 450°C to promote the formation of the crystal of sodium tungsten bronze. As the furnace temperature was increased, the crystallinity of the product samples was increased.

Fig. 8. Powder-XRD data of sample products obtained when the tube furnace was set at the temperature of (a) 600°C , (b) 500°C , (c) 450°C , and (d) 400°C (the highest tube temperature is given in bracket). The samples were produced at Na/W ratio of 1.0 and #2 flow rate of 0.5 L min^{-1} (standard liters per minute). #1 flow rate is zero. The moisture mass concentration in total flow is 0.046 g L^{-1} .

Comparison of Sodium Tungsten Bronze Products in Phases

To investigate sodium tungsten bronze particles in two phases, the micro morphologies of sodium tungsten bronze in the cubic and tetragonal phases are shown in Figs. 9(a) and 9(b), respectively. The cubic shape (Fig. 9(a)) and the orthogonal bar shape (Fig. 9(b)) of sample particles match well with the crystal lattice types of two typical samples. From the powder-XRD patterns in Figs. 9(c) and 9(d), it is found that all the peaks of the samples in both the cubic and tetragonal phases correspond very well with the reference positions of ICDD PDF 01-075-0232 and 01-070-0122. The sharp peaks indicate the excellent crystallinity of the samples. The cubic-phase sodium tungsten bronze has much high intensity of the peaks above the background, which is the evidence of better crystallinity than the tetragonal-phase bronze. Moreover, the calculated crystallinity of cubic and tetragonal phase of sodium tungsten bronze in Figs. 7(a) and 7(e) are 83% and 70%, respectively.

From the EDX data shown in Fig. 10, the Na:W:Cl ratio of the sample in the cubic phase is $\sim 0.72:1.00:0.02$ and $0.88:1.00:0.31$ for the sample in the tetragonal phase. Assuming all chlorine atoms come from NaCl, the Na:W ratio in the sodium tungsten bronze crystal of the cubic phase were $0.70:1.00$, and $0.57:1.00$ for the sample in the tetragonal phase. The molecular formulas for the cubic and tetragonal tungsten bronze are thus $\text{Na}_{0.70}\text{WO}_3$ and $\text{Na}_{0.57}\text{WO}_3$, respectively.

By comparing the lattice size of cubic-phase sodium tungsten bronze in ICDD database (Fig. S1 in ESI), a linear equation between lattice size and Na/W can be obtained. By submit the experimental value of cell size, 3.84 (from XRD) into the equation, the Na/W ratio can be calculated out as 0.732 , which is very near to the value of 0.70 ($\text{Na}_{0.70}\text{WO}_3$). Figs. 10(c) and 10(d) are the photos of cubic- and tetragonal-phase sodium tungsten bronze samples, respectively. The purple-red color of cubic-phase sample and the blue color of tetragonal-phase sample are in line with the summary of color vs. ion content by Granqvist (1995). The color difference of two sample is the consequence of different tungsten chemical status. Because of more sodium atoms occupying the lattice void, the average tungsten valence in the cubic-phase sample is lower than the tetragonal-phase one (Guo *et al.*, 2012c), which should be verified by the XPS in Fig. 11.

The XPS data for the sample products in the cubic and tetragonal phases is shown in Fig. 11 (without and with the sputtering). For the surface tungsten atom, the V valence tungsten was observed in the cubic-phase sample (Fig. 11(a)) while no such peak area is identified in the sample of tetragonal phase (Fig. 11(c)). After the sputtering, the XPS data of cubic-phase sample (Fig. 11(b)) shows larger area of V or IV valence tungsten than the tetragonal-phase one (Fig. 11(d)). The above evidences that the tungsten in the cubic-phase sample has more reductive status than the tetragonal-phase one, which is the cause for the different band structure for the light absorption in the visible range.

Fig. 12 shows the transmittance of sample particles in the cubic and tetragonal phases. It is found that the cubic-phase sodium tungsten bronze particles show better transmittance

Fig. 9. SEM images and XRD data of sodium tungsten bronze particle samples in the (a, c) cubic phase and (b, d) tetragonal phase, respectively.

Fig. 10. EDX data of sodium tungsten bronze for (a) cubic phase and (b) tetragonal phase. Photos of sodium tungsten bronze particles in the (c) cubic phase and (d) tetragonal phase when collected on the filter medium.

Fig. 11. XPS data of sodium tungsten bronze samples in the (a, b) cubic and (c, d) tetragonal phases without the sputtering and with the sputtering of 4 min.

Fig. 12. Transmittance of the sample sodium tungsten bronze products in the cubic and tetragonal phases (as the function of wavelength). The mass concentration of particle in the medium are kept the same.

in the visible light range than the tetragonal-phase one. One possible reason for the observation is that the high content of sodium ion in the cubic-phase sample makes it highly efficient in the dipole absorption of NIR. Another possible reason is that the impurity content, carbon and chlorine, in the cubic-phase sample (8.47 and 0.43 at%; Fig. 10(a)) are lower

than the tetragonal-phase one (9.90 and 5.97 at%; Fig. 10(b)). The other reason might be due to that the cubic-phase sample has the higher crystallinity, i.e., having less crystal boundary, compared with that of tetragonal-phase sample. The crystal boundary scatters the light, resulting in the reduction of transmittance.

CONCLUSION

A droplet-based synthesis process was developed to produce sodium tungsten bronze particles continuously in one step. This process consisted of atomizing the precursor solution into droplets, which were then carried by an N_2 flow and mixed with a second, partially saturated N_2 flow prior to entering a high-temperature tube furnace. Samples were subsequently collected at the exit of the furnace via filtration. Measuring the particle size distributions before and after the furnace heating stage, we found that each droplet served as a micro-reactor and produced one sodium tungsten bronze particle. We observed that the crystallinity was strongly related to the composition of the precursor solution—specifically, increasing the sodium content in the latter enhanced the former. This trend applied even as the furnace temperature was raised. Furthermore, given sufficient moisture content, the reaction resulted in only trace amounts of by-products (NaCl).

Exploring the involved particle formation mechanisms and chemical reactions in greater detail, we also discovered

the nearly complete evaporation of the methanol solvent from the individual droplets prior to their entry into the tube furnace. The resultant methanol vapor acted as a reductive regent in the reaction that occurred within each particle to facilitate crystallization.

By varying the Na/W ratio in the precursor solution, high-purity sodium tungsten bronze particles in the cubic phase ($\text{Na}_{0.70}\text{WO}_3$) and the tetragonal phase ($\text{Na}_{0.57}\text{WO}_3$) were produced. Particles in both phases demonstrated NIR shielding abilities.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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