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Original Research Paper

Synthesis of highly crystalline hexagonal cesium tungsten bronze nanoparticles by flame-assisted spray pyrolysis

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A B S T R A C T

Highly crystalline and hexagonal single-phase cesium tungsten bronze ($Cs_{0.32}WO_3$) nanoparticles were successfully synthesized by a flame-assisted spray pyrolysis followed by annealing under a reducing gas atmosphere. The resulting $Cs_{0.32}WO_3$ nanoparticles featured a pure hexagonal $Cs_{0.32}WO_3$ phase with a high crystallinity and homogeneous chemical composition. Unlike conventional methods, the proposed process in this paper has several advantages, including a short reaction time and the ability to yield products with high purity and good energy efficiency. Furthermore, the $Cs_{0.32}WO_3$ nanoparticles produced in this research showed a remarkable near-infrared shielding ability with a 97.7% cut-off at 1500 nm.

1. Introduction

Recently, near-infrared shielding materials have become highly desired for applications in solar control windows for automobiles and buildings to reduce the energy consumption of air conditioning. Noble metal nanoparticles (e.g., Ag [1] or Au [2]), semiconductor oxides (e.g., indium tin oxide (ITO) [3] or antimony tin oxide (ATO) [4]), black compounds, and rare-earth hexaborides show remarkably strong absorption of near-infrared light owing to the effects of localized surface plasmon resonances [5].

Tungsten bronze nanoparticles, such as tungsten trioxide doped with alkali metals, are promising candidates for applications to near-infrared shielding [6,7]. Takeda and Adachi found that tungsten bronze nanoparticles (M_xWO_3, M = Na, Tl, Rb, and Cs) produced by solid state reactions and milling methods have excellent optical properties [8]. The incorporation of the cations inside the WO_3 crystal structure also introduces free electrons, which are essential for enhancing the localized surface plasmon resonance. Hexagonal cesium tungsten bronze ($Cs_{0.32}WO_3$) nanoparticles are regarded as particularly promising for solar control window applications. Cesium ions have a plasmon resonant frequency that produces strong absorption in the near-infrared region and high transmittance in the visible region with a sharp gradient between the two regions [9].

To date, $Cs_{0.32}WO_3$ nanoparticles have been synthesized by solid state [8,10], hydrothermal [11], water controlled-release solvothermal [12], and thermal plasma [13] synthesis methods. Among these approaches, the solid state synthesis method has been widely used to produce $Cs_{0.32}WO_3$ nanoparticles on an industrial scale. However, this method involves many elaborate and multi steps, including heating under a H_2/N_2 atmosphere (e.g., at approximately 550 °C for 1 h), under a N_2 atmosphere (e.g., at approximately 800 °C for 1 h), and mechanical grinding (e.g., for 6 h) [8]. In addition, contamination occurring during the grinding step has also become a serious problem. Therefore, it is necessary to develop a simple and energy-efficient method for producing $Cs_{0.32}WO_3$ nanoparticles that is feasible for the large-scale synthesis of materials required for practical applications.

Flame-assisted spray synthesis (FASP) shows great promise as a process for continuous production of nanoparticles at a high rate. In the FASP process, the particle size, crystal size, and morphology of nanoparticles can be controlled by adjusting the gas flow rates and precursor concentration [14,15]. Owing to these advantages, a wide range of materials, from simple oxides to more complex

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functional materials, can be produced by the FASP method [16–19]. In this work, for the first time we report the synthesis of $Cs_{0.32}WO_3$ nanoparticles with the use of the FASP method by varying the methane (fuel) gas flow rates and investigate the effects of the flame temperature on the physical and optical properties of the so-formed nanoparticles. The as-synthesized $Cs_{0.32}WO_3$ nanoparticles were annealed at various temperatures under an H_2/Ar atmosphere to achieve a single $Cs_{0.32}WO_3$ phase. The near-infrared absorption properties of the as-synthesized $Cs_{0.32}WO_3$ nanoparticles before and after annealing were evaluated.

2. Experimental

2.1. Experimental setups

A schematic diagram of the experimental setups for the preparation of the $Cs_{0.32}WO_3$ nanoparticles is shown in Fig. 1. The FASP system [Fig. 1(a)] consisted of an ultrasonic nebulizer (NE-U17, Omron Healthcare Co., Ltd., Tokyo, Japan; operated at 1.7 MHz) for droplet formation, a diffusion flame burner (see Supporting Information Fig. SI-1), a glass flame reactor, and a bag filter for particle collection. Two precursors, i.e., an aqueous solution of 0.01 mol/L ammonium tungstate pentahydrate (ATP, $(NH_4)_{10}(W_{12}O_{41})\cdot 5H_2O$; Kanto Chemical Co., Inc., Japan; purity 88–90%) and an aqueous solution of 6.45 g/L cesium carbonate (Cs_2CO_3; Sigma-Aldrich Co., USA; purity 99.9%) were simultaneously supplied into the ultrasonic nebulizer by peristaltic pumps. The mixture of both precursors was immediately nebulized to prevent precipitation, and the generated droplets were subsequently fed into the central tube of the diffusion flame burner with a carrier gas (N_2; 3 L/min). Methane (CH_4) was used as the fuel gas, and its flow rate was varied from 0.5 to 3.0 L/min to investigate the effects of flame temperature on the obtained nanoparticles. The flow rate ratio of oxygen (O_2) to methane was maintained at 2.5 to ensure complete combustion. The as-synthesized nanoparticles were collected in a bag filter. During the experiment, the temperature inside the particle collector was maintained at 200 °C to avoid water condensation. To produce a single phase $Cs_{0.32}WO_3$, the as-synthesized particles were annealed inside a tubular furnace [Fig. 1(b)] [20,21]. The FASP-made nanoparticles were heated for 1 h at various temperatures at a heating rate of 400 °C/h under a 5%-H_2/Ar atmosphere based on the previously reported literatures [8,10,11]. After annealing, the nanoparticles were allowed to cool naturally.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apt.2018.07.001.

2.2. Characterization

A scanning electron microscope (SEM; S-5200, Hitachi, Tokyo, Japan; operated at 5–20 kV) and a transmission electron microscope (TEM; JEM-3000F, JEOL Ltd., Tokyo, Japan; operated at 297 kV) were used to investigate the size, morphology, and crystal structure of the as-synthesized nanoparticles. The crystal structures of the $Cs_{0.32}WO_3$ nanoparticles were also determined by X-ray diffraction (XRD; D2 PHASER, 40 kV and 30 mA, Bruker Corp., USA). The ATP powder and precipitates of the precursor mixture were characterized by thermogravimetric analysis (TGA; TGA-60, Shimadzu, Japan; at a heating rate of 10 °C/min and N_2 carrier gas flow rate of 50 mL/min). To characterize their optical performance, the as-synthesized $Cs_{0.32}WO_3$ nanoparticles were dispersed in methyl isobutyl ketone at a concentration of 0.02 wt% [9]. Optical measurements were performed using a UV–Vis-NIR spectrophotometer (Model V-670, JASCO Corporation, Japan).

3. Results and discussion

3.1. Effects of flame temperature on the formation and physical properties of $Cs_{0.32}WO_3$ nanoparticles

In general, the flame temperature of the reaction field in the FASP process is influenced by the flow rates of methane and oxygen [22]. Generally, a higher methane flow rate results in a higher

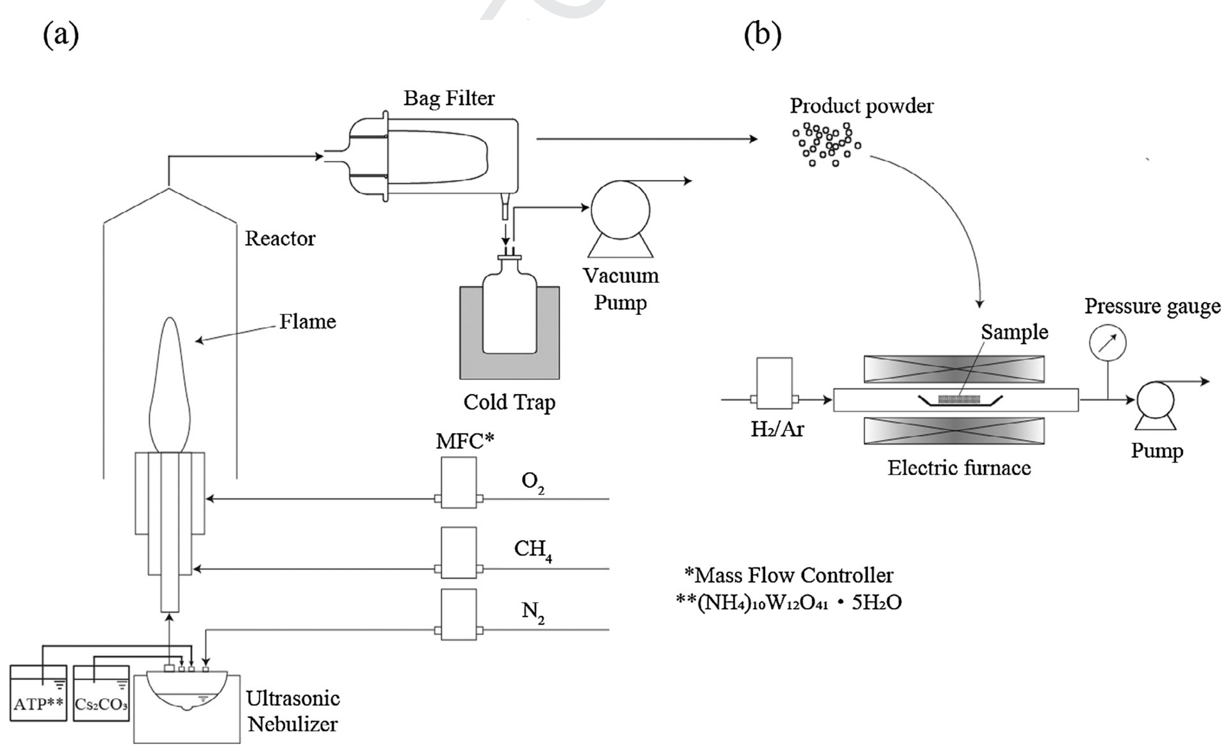

Fig. 1. Schematic diagram of experimental setup for (a) flame-assisted spray synthesis and (b) annealing processes.