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Preparation of quaternary tungsten bronze nanoparticles by a thermal decomposition of ammonium metatungstate with oleylamine

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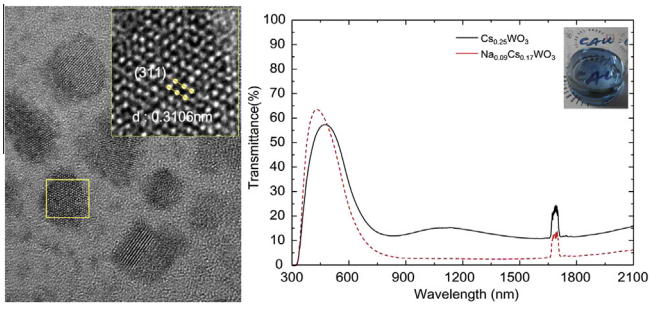
HIGHLIGHTS

- Tungsten bronze nanoparticles prepared via a thermal decomposition with oleylamine.
- Quaternary tungsten bronze nanocrystals doped with sodium and cesium were prepared.
- Sodium and cesium ions were intercalated into the cubic pyrochlore structure of WO_3.
- NIR absorption is broader and stronger than that of the equivalent ternary compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of quaternary tungsten bronze nanocrystals (QTBN) doped with sodium and cesium, $Na_xCs_yWO_z$, which were prepared via a simple thermal decomposition process involving the combination of ammonium metatungstates with oleylamine as both the surfactant and the solvent. The QTBN capped with oleylamine had an average diameter of about 30 nm and exhibited a shielding property of approximately 97% of near-infrared radiation across a wavelength range of 780–2100 nm, while transmitting 64% of visible light at 432 nm upon dispersion in a non-polar solvent of toluene. Our characterizations showed that both sodium and cesium ions could successfully be intercalated into the framework of the cubic pyrochlore structure of tungsten oxide at a relatively low reaction temperature and within a short time, generating the quaternary compound of tungsten bronze nanoparticles. As a result, our procedure conferred near infrared absorption properties upon the QTBN that are superior to those of ternary tungsten bronze nanoparticles in terms of absorption range and intensity, suggesting a significantly advanced solution process capable of producing useful near infrared absorbents.

1. Introduction

Over the last a few decades, the development of nanomaterials capable of effectively absorbing near-infrared radiation (NIR, wavelengths ranging from 780 to 2500 nm) from the sun in a range as wide as possible, has been a significant topic for various applications. Smart windows coated with NIR absorbents are able to prevent heat gain or loss, while being transparent for visible light, thereby reducing energy consumption by buildings or automobiles [1]. In addition, NIR absorbents are useful materials for solar collectors and optical filters [2]. Tungsten bronzes (M_xWO_3), which are tungsten trioxide compounds doped with alkali metals, have non-stoichiometric compositions with various structures, such as

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cubic, hexagonal, tetragonal, and pyrochlore [3]. These compounds are attractive NIR absorbents, due to their distinctive electrical and optical properties, which depend on their stoichiometric composition [4]. When alkali metals are intercalated into the framework formed by corner-sharing WO_6, the metal ions are believed to contribute their electrons to the conduction band of WO_3, forming surface plasmon polariton of free electrons and introducing empty, higher sub-bands or states in the conduction band [5–8]. In this regard, tungsten bronze nanoparticles are attractive NIR absorbing materials, because of their unique and highly desirable optical properties, namely, strong absorption in the NIR wavelength range based on sub-band energy levels, and transparency in the visible wavelength range [9–13].

Current technologies for synthesizing tungsten bronzes nanoparticles can mainly be classified into solid-state reactions and hydrothermal synthesis. The solid state reaction typically employs tungsten precursors and a heating process in a furnace at high temperatures over 500 °C, while exposed to a gas flow consisting of a mixture of H_2 and N_2 to obtain products in the reduced state [11]. However, this conventional process is considered to be risky, because of the use of hydrogen gas. Furthermore, the process is also time-consuming because of the mechanical milling procedure required to reduce the particle size from micro- to nanometer scale to increase the availability of free electrons on the surface by increasing the surface area. On the other hand, the hydrothermal synthesis method utilizes chemical reactions at a temperature below 250 °C without requiring mechanical milling. However, the hydrothermal method requires the use of tungstate salts, dissolved in water or ethanol [14], in which case the reaction has to be performed in a high-pressure reactor with a reaction time exceeding 18 h, because the reaction temperature exceeds the boiling points of the solvents. In addition, the resulting products require a reduction process to achieve conversion to the reduced state, because they are readily oxidized by oxygen in polar solvents [15,16]. Thus, the development of an advanced technology that would enable the direct synthesis of nanocrystals of tungsten bronzes in the reduced state via a solution-based process [17] utilizing relatively mild reaction conditions and shorter reaction times would be highly desirable. Furthermore, it would also be necessary to synthesize the nanocrystals of tungsten bronze such that they exhibit a wide NIR absorption range to compensate for the fact that ternary compounds of tungsten bronzes, that is, tungsten trioxides doped with an alkali metal, typically only exhibit strong NIR absorption over a limited range of wavelengths.

In this paper, we report a simple process to synthesize quaternary tungsten bronze nanoparticles (QTBN) in the reduced state by using a simple, convenient, reproducible route in which we employ oleylamine to provide nanocrystals of NIR absorbents with a broad working waveband. A previous report of ours described the use of a solid state reaction and a conventional mechanical milling process to produce nanocrystals of quaternary tungsten bronzes doped with sodium and cesium, which displayed remarkably improved NIR shielding properties in comparison to ternary cesium tungsten bronze [18]. This study demonstrates the facile synthesis of the quaternary compound of sodium cesium tungsten bronze nanoparticles, via a one-pot process, to maximize their NIR shielding properties. The synthesis of inorganic nanocrystals solely using oleylamine is well known, but has never been explored for preparing nanocrystals of tungsten bronzes.

2. Experimental

2.1. Materials

Ammonium metatungstate hydrate (AMT, $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$), cesium hydroxide monohydrate ($CsOH\cdot H_2O$), oleylamine (>70%), and toluene were purchased from Sigma–Aldrich. Sodium hydroxide (NaOH) and acetone were purchased from Samchun Chemical. All reagents used in this study were analytical reagent grade and were used as received.

2.2. Nanoparticle synthesis

A slurry was prepared by adding 0.1 mmol (0.2956 g) of AMT to 20 mL oleylamine with magnetic stirring, after which a pre-determined amount of alkali metal precursors was added to produce Cs_yWO_z and $Na_xCs_yWO_z$, which was stirred for 1 h (Table 1). The suspension was transferred to a three-neck round-bottomed flask connected to a reflux condenser. The atmosphere in the reactor was replaced with nitrogen gas by purging for an hour, following which the flask was heated at 250 °C under stirring while maintaining the nitrogen atmosphere. After 2 h the reaction was observed to be complete and the reaction mixture was allowed to naturally cool down to room temperature. The precipitate was collected by using centrifugation for 15 min at 8000 rpm, after which it was washed twice with acetone to remove the excess oleylamine. The collected precipitate was then magnetically stirred with acetone for 2 h to re-disperse the agglomerated nanoparticles, subsequent to which it was dried at room temperature. After drying, the powder was suspended in solvents such as toluene, hexane, and chloroform for the analysis of its characteristics (see Fig. 1).

2.3. Characterization of tungsten bronze nanoparticles

The crystal structures of the tungsten bronze nanoparticles were identified by X-ray diffraction (XRD, Bruker-AXS NEW D8-Advance). The morphology and structure of the samples were studied using field emission transmission electron microscopy (FE-TEM, FEI Tecnai G2 F30 S-Twin). The particle size distribution of the tungsten bronze nanoparticles was determined by Dynamic Light Scattering (Nano partica SZ-100 series, Horiba Scientific) at a temperature of 25 °C with a scattering angle of 90°. The compositions of the particles were estimated by energy dispersive spectroscopy (EDS, Thermo Scientific NORAN System 7) and X-ray photoelectron spectroscopy (XPS, $h\nu$ = 1486.6 eV Al Kα). The existence and quantity of oleylamine on the surface of the tungsten bronze nanoparticles were investigated using Fourier transform infrared (FT-IR, OTSUKA ELS-Z) spectroscopy and thermogravimetric analysis (TGA, Scinco TGA N-100). Absorption and transmittance spectra were obtained using a spectrophotometer (JASCO V-670) in the range of 300–2100 nm.

3. Results and discussion

3.1. Crystal structure of tungsten bronze nanoparticles (TBN)

The QTBN were successfully synthesized by mixing AMT (as the tungsten precursor), and cesium and sodium hydroxide (as the alkali metal precursors) in oleylamine, followed by heating at 250 °C for 2 h; that is, a mild reaction temperature and a short reaction time. The crystal structures of the resulting products were

Table 1
The molar ratios in which the elements were mixed for synthesizing cesium tungsten bronze and sodium cesium tungsten bronze nanoparticles based on 1 mol tungsten.

Sample	Concentration (mmol)		
	Na	Cs	W
Cs_yWO_z	0	0.33	1
$Na_xCs_yWO_z$	0.11	0.22	1