Thermal Plasma Synthesis of Tungsten Bronze Nanoparticles for Near Infra-Red Absorption Applications

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Supplementary Information

Experimental.

Materials Synthesis: The thermal plasma synthesis of alkali tungsten bronze nanoparticles was performed in a multi-purpose RF plasma reactor such as shown in Supporting Information Figure 1. The unit consists of a water cooled plasma torch (Model PL-50, 3 MHz, Tekna Plasma Systems Inc.), a reaction chamber, and powder collection units. A powder mixture containing a desired molar ratio of M/W was prepared from a physical mixture of ammonium paratungstate (APT, Global Tungsten & Powders Corp., -40 mesh) with an alkali metal salt such as sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$, Alfa Aesar), cesium formate monohydrate ($CsCOOH \cdot H_2O$, Cabot Specialty Fluids), potassium carbonate (K_2CO_3, Alfa Aesar), tri-potassium citrate monohydrate ($C_6H_5K_3O_7 \cdot H_2O$, Alfa

Aesar) or potassium acetate (CH_3CO_2K, Alfa Aesar). The APT powder mixture was entrained in a carrier gas flow (argon, 7 slpm) with a standard powder feeder at a rate of 0.7 to1 kg/h. The fluidized powder mixture was axially injected through a Tekna SD 260 dispersion probe at the coil center of the induction plasma torch operating at 65 kW while the sheath gas composition was held at 100 slpm Ar, 5 slpm He, and 1 slpm H_2 [slpm = standard liters per minute; standard conditions for the calculation of slpm are defined as: Tn 0°C (32°F), Pn = 1.01 bar (14.72 psi)]. The operating pressure in the reactor unit was maintained at slightly lower than atmospheric pressure (700 torr) by means of a vacuum pump. The produced tungsten bronze nanopowders are collected by a filter bag after passing a heat exchange zone.

Characterization: For powder X-ray diffraction (PXRD) analysis, the samples were gently packed into deep 1.0 mm aluminum-sample holders and the excess on the surface was cut off with an edge to minimize the expected preferred orientation. Some samples were additionally prepared from a suspension in isopropyl alcohol deposited onto a zero-background Si-plate. Due to the high linear absorption of X-rays from the tungsten bronzes, they all have a μ of approximately 1000 cm^{-1} which means that the depth of penetration is only 1 to 4 μm. Thus, even thin films of these materials should be considered as sufficiently thick for optimal diffraction and reliable quantitative results. The samples were run on a standard Bragg-Brentano Siemens D5000 Diffractometer system. A high-power, line-focus Cu-target was used, operating at 50kV/35mA. The data were collected on a step scan mode with step size 0.02° 2-theta and counting time of 2.5 seconds per step. The data processing was done by Diffrac *Plus™* software Eva™ v. 8.0. The primary phase identification was performed using SearchMatch *™* and PDF-2 reference database[1] where some of the possible M_xWO_3 compounds were found. The missing references were created as simulated x-ray patterns from single crystal structural data retrieved from ICSD database.[2] The profile fitting and Rietveld analyses were carried out by Bruker's AXS Topas™ profile fitting software v. 2.1. Field emission scanning electron microscopy (FE-SEM) was performed using a Hitachi S-5200 in-lens SEM. Samples were prepared from isopropanol dispersions which were deposited onto a 200 mesh copper grid with formvar carbon

support film. For UV-vis-NIR spectroscopy, the tungsten bronze nanopowders were first mixed with

KBr at a loading of 0.25 wt.-% then finely ground with mortar and pestle. KBr pellets were

fabricated using a FTIR die and Carver® press at 15000 pounds for 1 minute. Blank KBr pellets were

fabricated for the collection of background spectra. Transmission spectra were collected on a Cary

5000 UV-vis-NIR spectrophotometer. All the spectra reported here are the absorption spectra with

background correction selected. The spectra were collected from 2500 nm to 200 nm with a scan rate

of 600 nm per min. BET surface area measurements were performed on a Quantachrome Nova 1000.

Samples were outgassed at 110°C for 1h. A 5 point BET was collected.
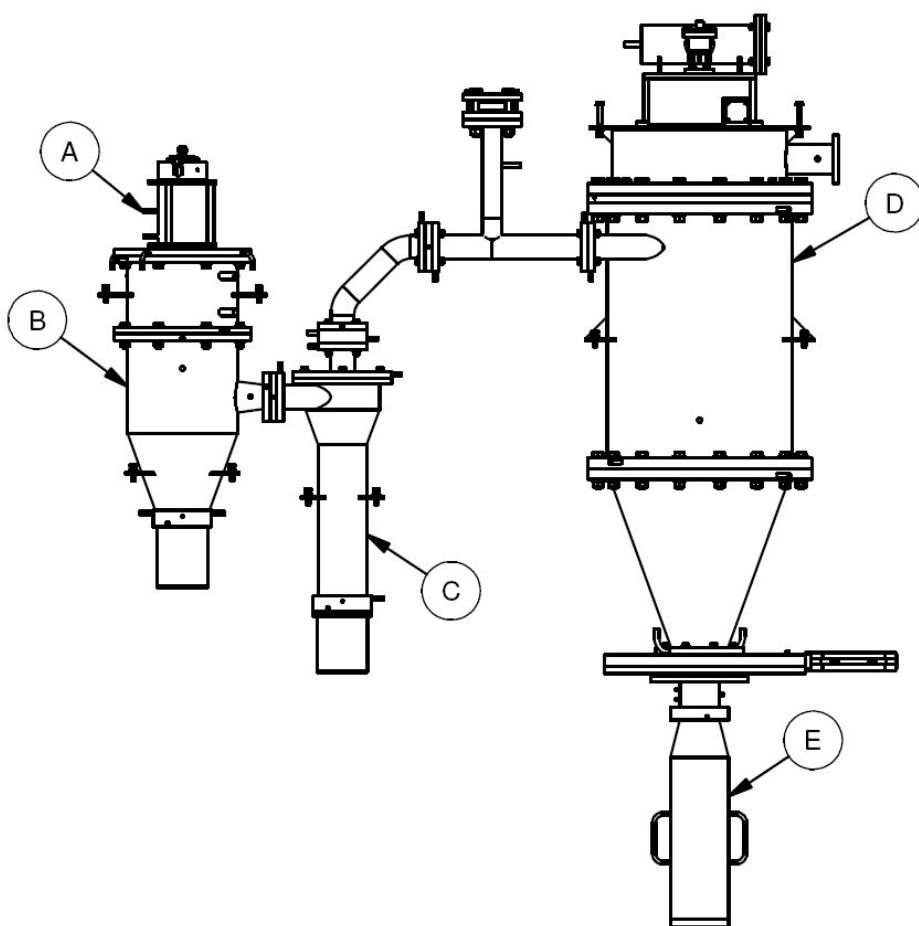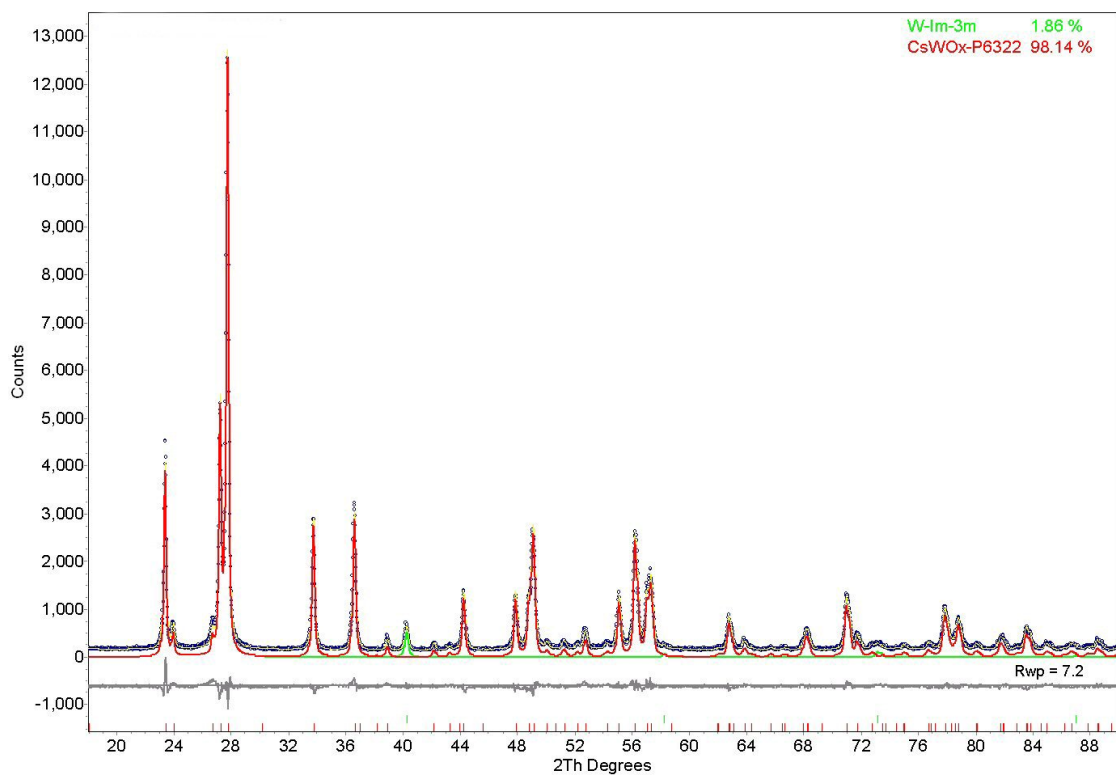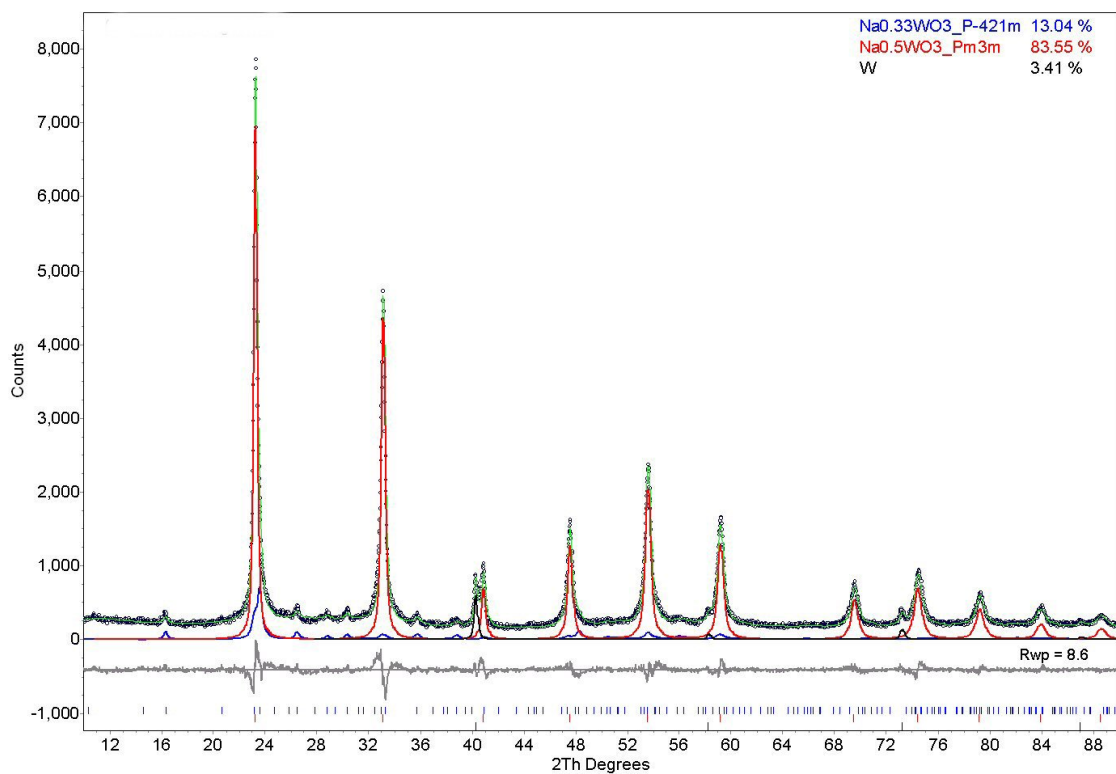

Fig. S1. ICP reactor design for the synthesis of tungsten bronze nanoparticles. The labeled components are as follows: A) TEKNA PL-50 plasma torch, B) reactor, C) cyclone, D) filter baghouse, and E) nanopowder collection canister.
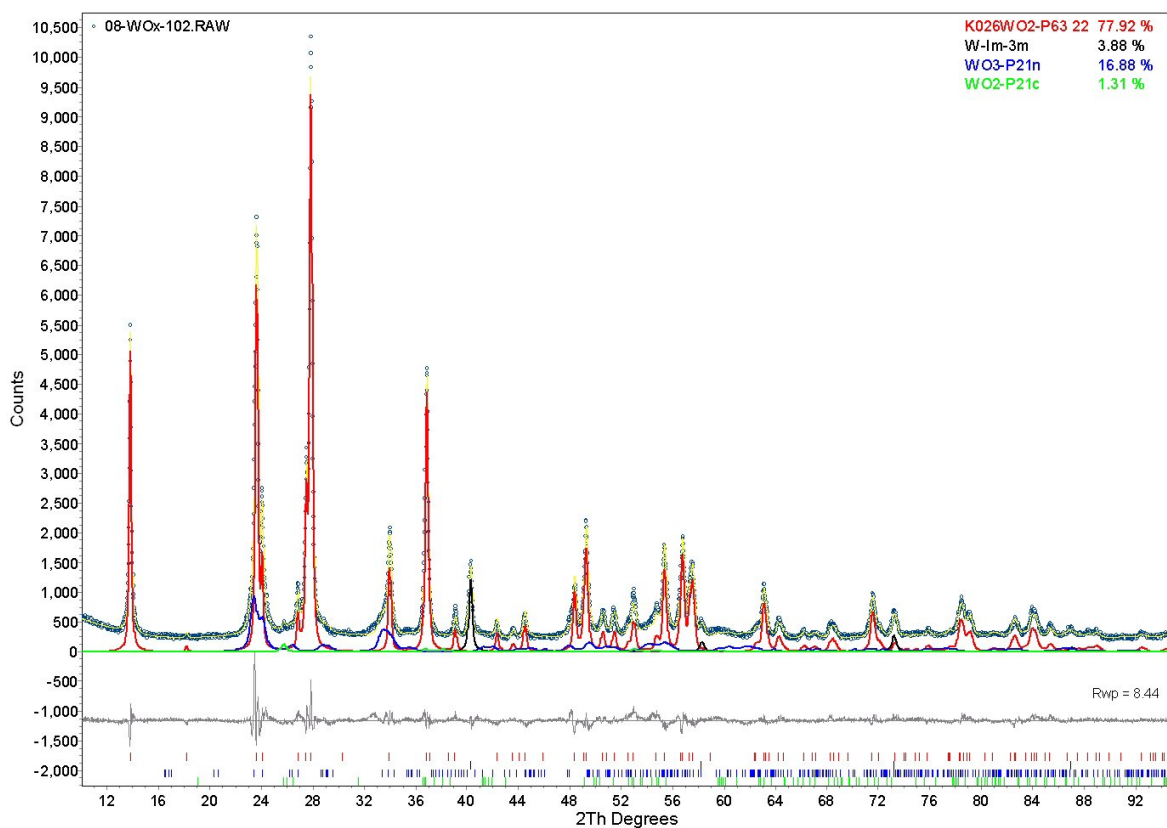
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Fig. S2. Rietveld refinement plots for $Na_{0.38}WO_3$ (top) and $Cs_{0.2}WO_3$ (middle) and $K_{0.26}WO_3$ (bottom) produced by thermal plasma synthesis.

Material	M/W ratio	Space Group	BET SA (m^2/g)	Particle size (nm)	L_v (nm)
NIR-Na	0.33	Pm3m	8.5	93	72
NIR-K	0.26	$P6_322$	16.5	49	43
NIR-Cs	0.30	$P6_322$	15	48	39

Table S1. Material properties of thermal plasma synthesized tungsten bronze nanopowders.

REFERENCES.

1. Powder Diffraction Reference Database, Release 2001, ICDD, Southmore, Pennsylvania.

2. .Inorganic Crystal Structure Database, 2005-2, Karlsruhe, Germany.