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

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**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$_2$CO$_3$·H$_2$O, Alfa Aesar), cesium formate monohydrate (CsCOOH·H$_2$O, Cabot Specialty Fluids), potassium carbonate (K$_2$CO$_3$, Alfa Aesar), tri-potassium citrate monohydrate (C$_6$H$_5$K$_3$O$_7$·H$_2$O, Alfa...
Aesar) or potassium acetate (CH₃CO₂K, 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 to 1 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 H₂ [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 database¹ where some of the possible MₓWO₃ 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.
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.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>M/W ratio</th>
<th>Space Group</th>
<th>BET SA (m$^2$/g)</th>
<th>Particle size (nm)</th>
<th>$L_v$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIR-Na</td>
<td>0.33</td>
<td>Pm3m</td>
<td>8.5</td>
<td>93</td>
<td>72</td>
</tr>
<tr>
<td>NIR-K</td>
<td>0.26</td>
<td>P6$_3$22</td>
<td>16.5</td>
<td>49</td>
<td>43</td>
</tr>
<tr>
<td>NIR-Cs</td>
<td>0.30</td>
<td>P6$_3$22</td>
<td>15</td>
<td>48</td>
<td>39</td>
</tr>
</tbody>
</table>

REFERENCES.


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