Supplementary Material (ESI) for Journal of Materials Chemistry

Support Information

Novel Synthesis of Homogenous Cs_xWO_3 Nanorods with Excellent NIR Shielding Properties by a *Water Controlled-Release Solvothermal Process* (WCRSP)

Chongshen Guo[a], Shu Yin[a], Peilin Zhang[a], Mei Yan[b], Kenji Adachi[c], Takeshi Chonan[c], Tsugio Sato[a]

Institute of Multidisciplinary Research for Advanced Materials ,Tohuko University, 2-1-1 Katahira,Aoba-ku ,Sendai,Japan[a]

Department of Chemistry, Graduate school of Science, Tohuko University, Aoba-ku, Sendai Japan[b]

Ichikawa Research Laboratory, Sumitomo Metal Mining Co., Ltd, Japan[c]

Nanosize homogenous rod-like of tungsten bronze type Cs_xWO_3 with excellent NIR shielding ability was successfully synthesized by a novel and facile water controlled-release solvothermal process

Experimental

Analytical grade chemicals, such as Tungsten hexachloride (WCl_6), Cesium hydroxide monohydrate ($CsOH \cdot H_2O$), dehydrated ethanol and acetic acid, purchased from Kanto Kagaku Co.Inc. without further purification were used as starting materials. In a typical experiment, certain amount of WCl_6 was dissolved into the dehydrate ethanol with violently stirring, then the desired amount of CsOH was introduced to the above yellowish solution of WCl_6. After the mixture become homogeneous, 10ml acetic acid was introduced. The final concentration was adjusted to 0.015M of WCl_6 with 33 at.% of CsOH. The mixture solution was introduced into a Teflon-lined autoclave of 100 ml internal volume, followed by solvothermal treatment at 200^{o}C for 20h.

This method, which is named as *water controlled-release solvothermal process(WCRSP)*, is a novel and facile method to synthesize nanorods of tungsten bronze type Cs_xWO_3. Water molecules were released slowly by the reaction between acetic acid and dehydrate ethanol during the solvothermal process. Dark blue colored products were centrifuged and washed with water and ethanol for 4 times, respectively, followed by vacuum drying at 60^{o}C over night. It is definite that the Cs source of $CsOH \cdot H_2O$ contained little amount of H_2O .But what is notable, the initial atomic ratio of $CsOH \cdot H_2O$ to WCl_6 is just 0.5, that is, the water molecules contained in Cs source are just half of WCl_6 .It is not enough for the hydrolysis of total WCl_6 molecule and the effects of water molecules contained in Cs source can be negligible (hydrolyze one molecule of WCl_6 need six water molecules to participate). Due to the poor solubility in the mixed-solvent of ethanol and acetic acid, CsCl and Cs_2SO_4 are not effective Cs sources in the present *WCRSP* process.

The coating slurry was formed by mixing the Cs_xWO_3 powder with collodion and ethanol at a mass ratio of ethanol: collodion: Cs_xWO_3=1:0.93:0.15. Then the coating slurry was painted on a quartz glass by an applicator with concave in depth of 12.5μm. The phase compositions of the samples were characterized by X-ray diffraction analysis (XRD, Shimadzu XD-1) using graphite-monochromized *CuKα* radiation. The size and shape of the nannoparticles were observed by transmission electron microscopy (TEM, JEOLJEM-2010). The particle distribution was analyzed by laser diffraction particle size analyzer (Shimadzu SALD-7000). The optical response of the thin film was measured by using a spectrophotometer (JASCO V-670), giving output of transmittance in the UV, visible, and infrared ranges (200-2700nm). Energy-dispersive X-ray spectrometer (EDXS) was employed for approximate elemental analyses.

Table S-1 .The composition of solvent* before and after solvothermal reaction

	Ethanol	Acetic acid	Acetyl acetate	Ethyl ether	H_2O
Before	0. 686mol	0.175mol	**0**	0	0
After	**0.455** mol	**0.023** mol	**0.152** mol	**0.031** mol	**0.123**mol

* analyzed by NMR

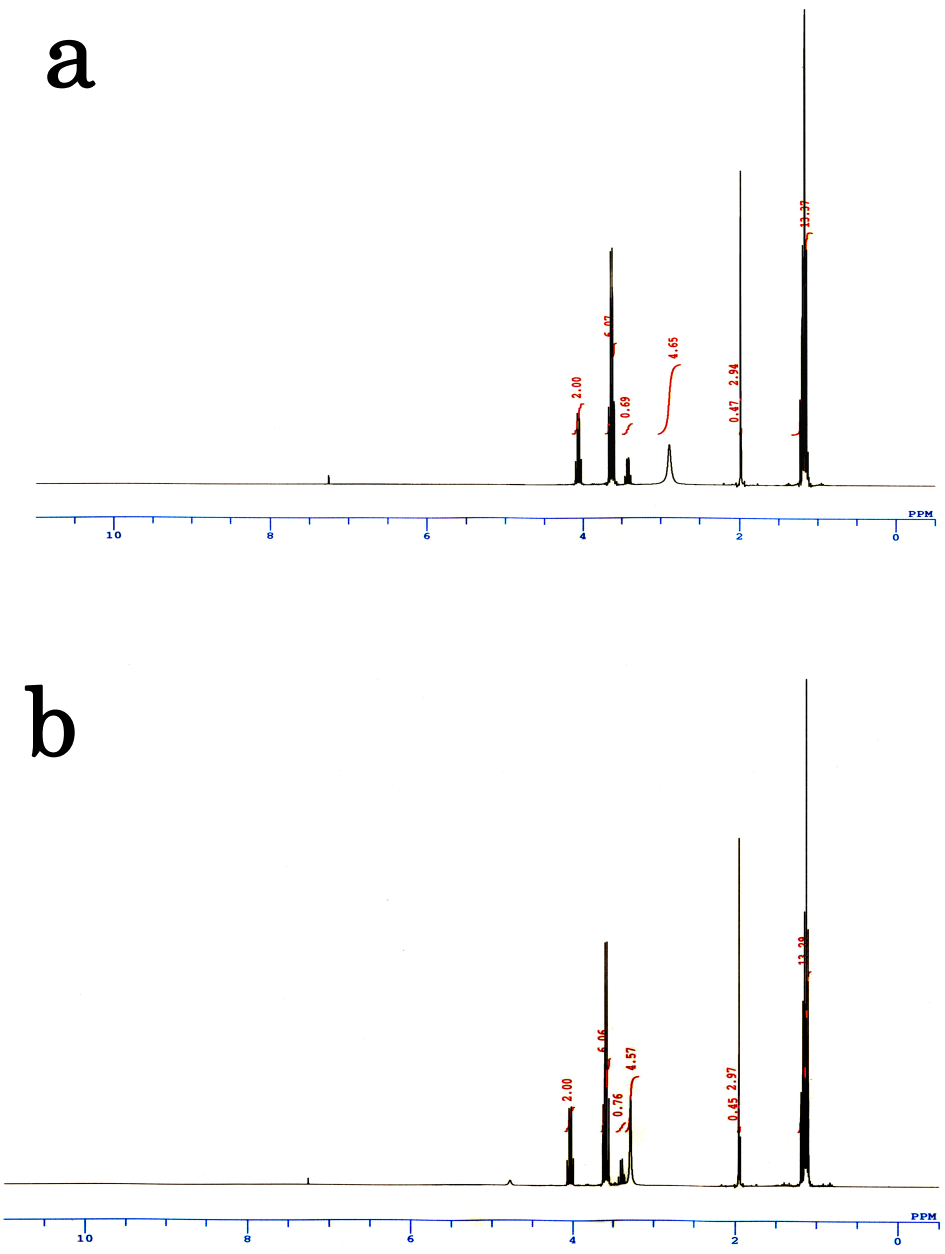

Fig. S-1 The NMR spectra of (a) the solvent after solvothermal reaction; (b) the reference solution with the composition listed in Table S-1

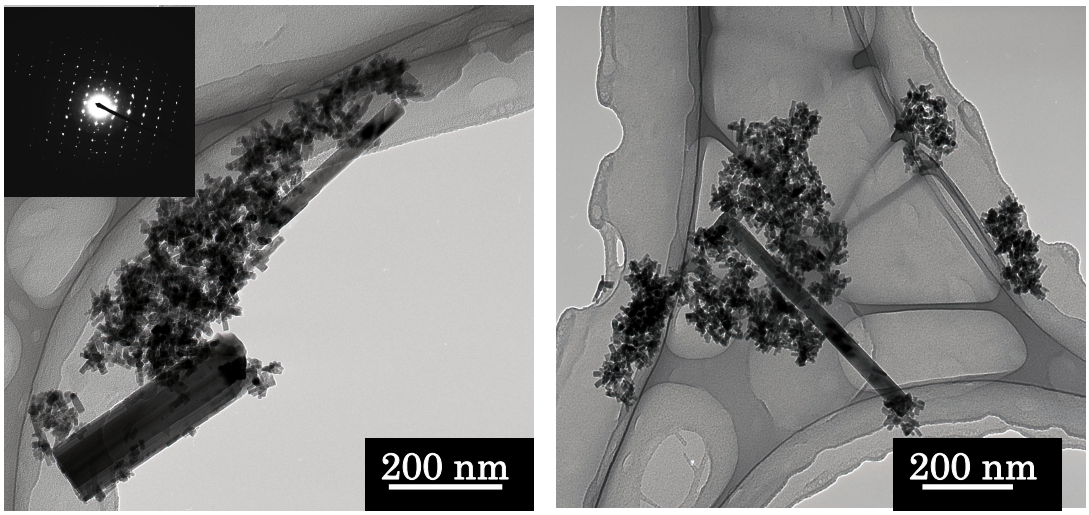

Fig. S-2 TEM image of product synthesized by *non controlled-release process* using the mixture solvents of ethanol and water. The amount of water *(0.123mol, 2.214g)* used in the synthesis was set as the same with that released from the WRCP process (without water additive in advance). The inset showed the ED pattern.

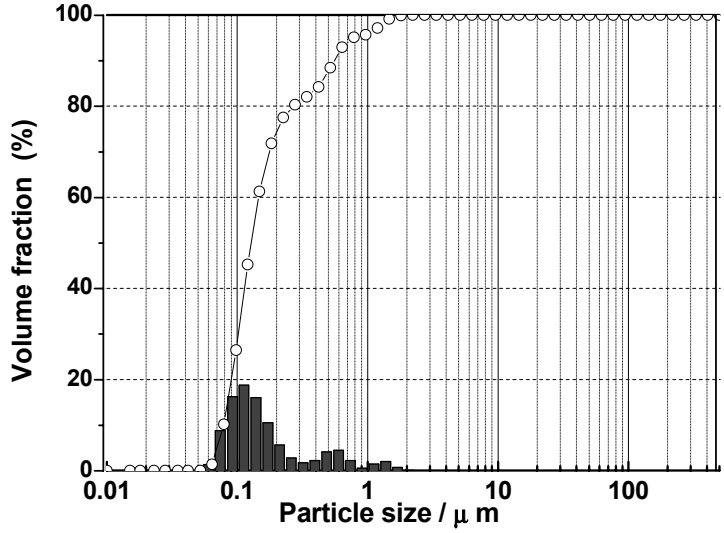

Fig. S-3 Particle size distribution of the product synthesized from *non controlled-release process.* The amount of water *(0.123mol, 2.214g)* used in the synthesis was set as the same with that released from the WRCP process (without water additive in advance).

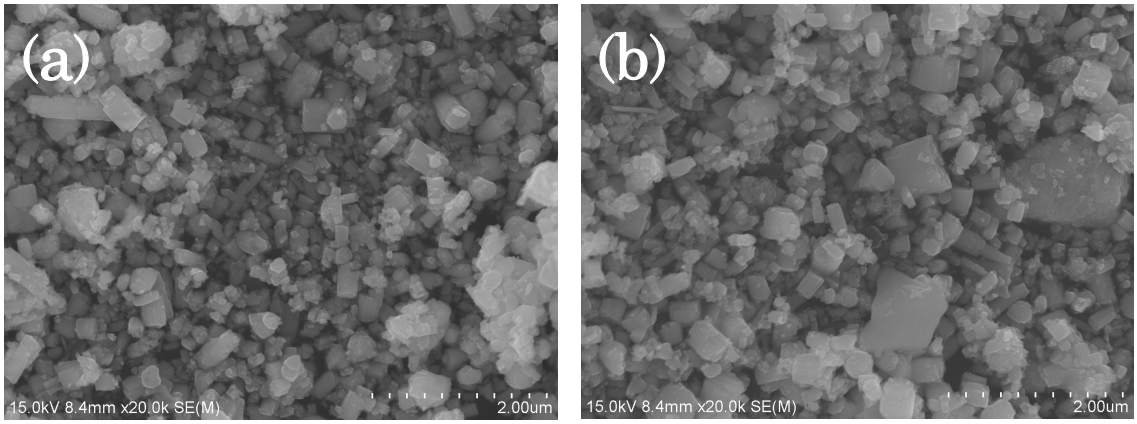

Fig. S-4 SEM image of product synthesized by hydrothermal reaction (a)before and (b) after H_2 reduction at 550^{o}C for 1h.

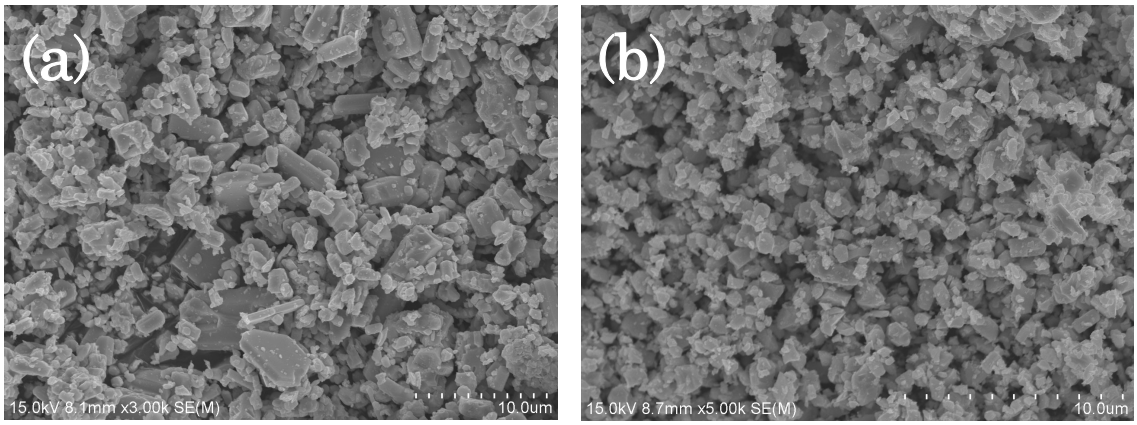

Fig. S-5 SEM images of products synthesized by solid-phase reaction (a)before and (b) after ball-milling treatment.

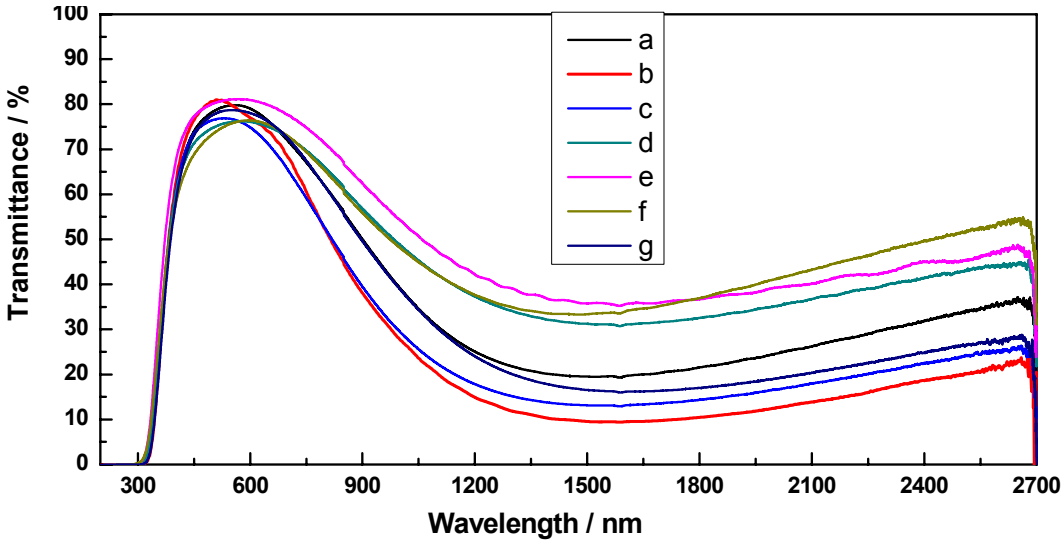

Fig. S-6 The transmittance spectra of Cs_xWO_3 obtained by employing different solvents.
(a)0.175 mol methanoic acid +0.69mol ethanol; (b) 0.175 mol acetic acid +0.69mol ethanol;
(c) 0.175 mol propanoic acid +0.69mol ethanol; (d) 0.175 mol butyric acid +0.69mol ethanol;
(e) 0.175 mol n-pentanoic acid +0.69mol ethanol; (f) 0.175 mol decanoic acid +0.69mol ethanol;
(g) 175 mol acetic acid +0.69mol propanol.