Novel synthesis of homogenous Cs_xWO_3 nanorods with excellent NIR shielding properties by a water controlled-release solvothermal process†

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

There has been great demand for materials which shield near-infrared (NIR, wavelength of 780 to 2500 nm) radiation (heat rays) by employing transparent coating on the windows of automobiles, buildings, *etc.*,[1] in order to reduce energy consumption of air conditioning and thereby decrease the emission of carbon dioxide. For the application as heat ray shielding materials, an excellent shielding ability of NIR rays as well as high visible light transparency is required. It is well known that nanoparticles of noble metals,[2] black compounds,[3] rare-earth hexaborides,[4–6] tin-doped indium oxide (ITO)[7,8] *etc.*, can shield NIR due to the effect of the plasma vibration of the free electrons. However, each of them has its own drawbacks. The films consisting of noble metal or black compounds show low visible light transparency.[2,3] The rare-earth hexaborides shield only certain wavelengths of IR rays and do not shield the whole extent of NIR rays.[4–6] In addition, high temperature (*ca.* 1500 °C) and vacuum conditions are necessary for the syntheses of rare-earth hexaborides. It exhausts much energy to crush the rare-earth hexaborides particles because of their hardness. Tin-doped indium oxide (ITO) film is a famous transparent conductive film with heat-ray shielding effect,[9–12] however, it can only shield the IR rays of wavelength longer than 1500 nm.[10] In addition, indium is one of the expensive rare metal resources.

Adachi *et al.* reported that the nanoparticles of caesium bronze (Cs_xWO_3) with a hexagonal structure (Fig. 1(A)) showed promising performance as solar filters.[5] They prepared the hexagonal caesium tungsten bronze nanoparticles by traditional solid state reaction in H_2–N_2 gas atmosphere around 800 °C, followed by milling for long times. It was also reported that the hexavalent tungstate with a general formula of $A_xWO_{3+x/2}$[13,14] could be prepared by hydrothermal reactions. The compound showed very similar XRD profiles to tungsten bronze (A_xWO_3), however, did not show NIR absorption ability because of the lack of free electrons. Therefore, the additional heat treatment under H_2 atmosphere was necessary to reduce $A_xWO_{3+x/2}$ to A_xWO_3. Such heat treatment resulted in the increase in the grain size and inhomogenity of the morphology of the particles.

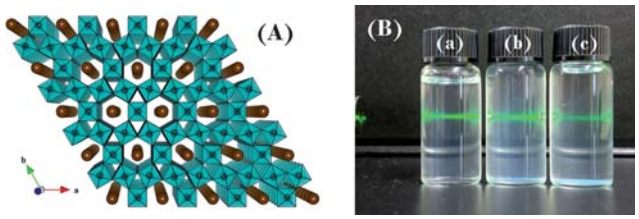

Fig. 1 (A) The structure of Cs_xWO_3 framework projected on a–b planes; (B) the Tyndall effect of the as-prepared sample dispersed in (a) water, (b) ethanol and (c) hexane.

In this paper, a new facile method to synthesize tungsten bronze type Cs_xWO_3 nanorods possessing excellent NIR shielding ability was developed by employing a water controlled-release solvothermal process (WCRSP), where after mixing WCl_6 ethanol solution and CsOH ethanol solution, the mixed solution and a desired amount of CH_3COOH was placed in a Teflon-lined autoclave and heated at 200 °C for 20 h. The product could be dispersed well in solvents and showed Tyndall effect (Fig. 1(B)), indicating the existence of nanoparticles.

All the XRD peaks of the sample could be indexed as the hexagonal caesium tungsten bronze $Cs_{0.32}WO_3$ (JCPDS file No. 831334) and no impurity peak was observed (Fig. 2(a)). The product showed the average particle size of 85 nm with a narrow particle size distribution (Fig. 2(b)).

Fig. 3 shows the TEM, HRTEM, SED and EDS of the product. The typical images showed the softly agglomerated homogenous nanorods with 15 nm in diameter and 40–50 nm in length. The chemical composition analysis based on the EDS (Fig. 3d) indicated the existence of Cs and W elements with the atomic ratio of Cs : W = 0.317 : 1, which is very close to the typical hexagonal tungsten bronze structure of $Cs_{0.32}WO_3$.

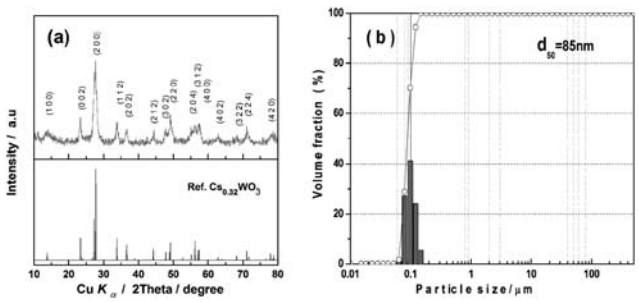

Fig. 2 (a) XRD pattern and (b) particle size distribution of the prepared sample (reference: $Cs_{0.32}WO_3$, JCPDS No. 831334).

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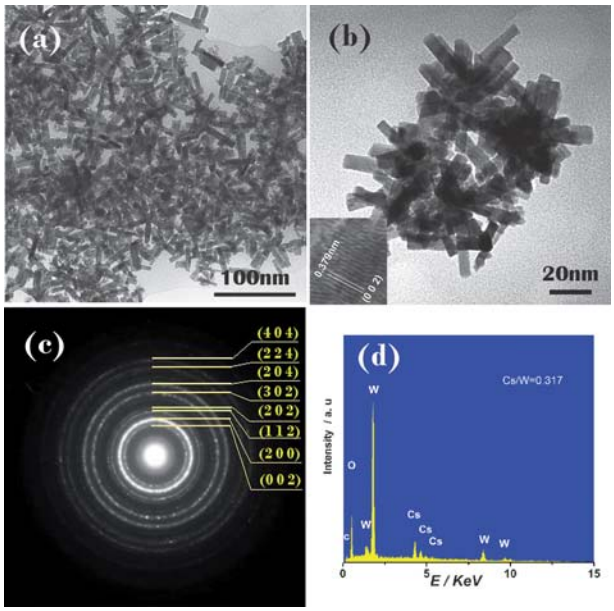

Fig. 3 (a) TEM (b) HRTEM images (c) ED pattern (d) EDS pattern of $Cs_{0.32}WO_3$ product.

In order to confirm the formation mechanism of the caesium tungsten bronze under present reaction conditions, the component of the mother liquid after reaction was analysized by NMR (Fig. S1†). The starting solution consisted of 0.986 mol ethanol and 0.175 mol acetic acid, whereas the solution after reaction consisted of 0.455 mol ethanol, 0.023 mol acetic acid, 0.152 mol acetyl acetate, 0.031 mol ethyl ether and 0.123 mol water. These results suggested that two reactions, esterification reaction between ethanol and acetic acid shown by eqn (1) and dehydration condensation reaction of ethanol shown by eqn (2), proceeded. The equilibrium constant of eqn (1) and (2) were determined as $K_1 = 1.8$ and $K_1' = 0.018$. Since there was no water molecule before reaction, the water molecules were generated by both esterification and condensation reactions. The water generated by the WCRSP process as well as ethanol might play an important role in the formation of Cs_xWO_3 nanorods as shown by eqn (3) and (4).

$$CH_3CH_2OH + CH_3COOH = CH_3CH_2OOCCH_3 + H_2O \; K_1 \quad (1)$$

$$2CH_3CH_2OH = CH_3CH_2OCH_2CH_3 + H_2O \; K_1' \quad (2)$$

$$WCl_6 + 3H_2O = WO_3 + 6\,HCl \quad (3)$$

$$WO_3 + x\,CsOH + x/4\;C_2H_5OH = Cs_xWO_3 + x/4\;CH_3COOH + 3x/4\;H_2O \quad (4)$$

For comparison, caesium tungsten bronze was formed by adding the same amount of water in the starting solution, and it was confirmed that the product consisted of irregular sized particles (Fig. S2 and S3†). Since the grain growth and the agglomeration of the metal oxide particles synthesized in ethanol are much lower than those in water, the WCRSP process seems to be important to generate the well dispersed uniform size of caesium tungsten bronze nanorods. The directional absorption of slowly released water on the initially formed nanoparticles and the intrinsic growth tendency along

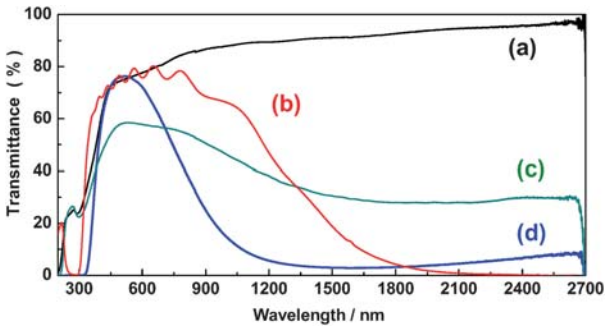

Fig. 4 Transmittance spectra of (a) pure WO_3 without Cs insertion; (b) commercial ITO glass (10 Ω/□); (c) $Cs_{0.32}WO_3$ obtained by hydrothermal reaction according to Michailovski's method[13] followed by H_2 reduction process at 550 °C for 1 h; (d) $Cs_{0.32}WO_3$ synthesized by the WCRSP process without any additional treatment.

c-axis of hexagonal-phase substance maybe the reasons for the formation of one-dimensional nanorods.

Tungsten trioxide (WO_3) possessed a wide band gap of 2.62 eV and was transparent in visible and NIR lights range (Fig.4a). Fig. 4 (b–d) shows the transmittance profiles of $Cs_{0.32}WO_3$ synthesized by the WCRSP process, $Cs_{0.32}WO_3$ obtained by hydrothermal reaction followed by H_2 reduction process and ITO glass, where the $Cs_{0.32}WO_3$ powders obtained by hydrothermal reaction followed by H_2 reduction process were dispersed using a wet-type particles dispersing apparatus (Sugino Machine, STAR BURST MINI) (Fig. 4c), but $Cs_{0.32}WO_3$ synthesized by the WCSRP process was used as prepared without any particle dispersion treatment (Fig. 4d). It can be seen that $Cs_{0.32}WO_3$ synthesized by the WCRSP process showed excellent shielding ability of NIR rays of the wavelength above 800 nm and high transparency in the visible light. In contrast, $Cs_{0.32}WO_3$ obtained by hydrothermal reaction followed by H_2 reduction process and by solid–phase reaction[5] also showed NIR shielding ability, however, the NIR shielding performance and visible light transparency were much lower, probably due to the difference in the microstructure consisting of inhomogeneous much larger particles (Fig. S4 and S5†). ITO glass showed excellent visible light transparency, but the shielding ability of NIR of the wavelength less than 1500 nm was modest. The strong and broad NIR absorption property of $Cs_{0.32}WO_3$ bronze synthesized by WCRSP process might be related to its homogeneous rod-like morphology, small particle size and its related electronic structure. Similar bronze structure of Na_xWO_3 also shows excellent NIR absorption properties, which are thought to be related with the plasmon resonance of free electrons,[15] interband transition,[16] and small polarons.[17] It is expected that the nanorods exhibit transverse and longitudinal surface plasmon resonances that correspond to electron oscillations perpendicular and parallel to the rod length direction, respectively.[18] Compared with Cs_xWO_3 nanoparticles,[5] the homogeneous $Cs_{0.32}WO_3$ nanorods synthesized by the present WCRSP process exhibited superior performance as NIR shielding materials.

Other combinations of fatty alcohols and acids were also used to synthesize the Cs_xWO_3 in a similar manner, however, the sample synthesized from a mixed solvent of ethanol and acetic acid showed the best performance as a solar filter (Fig. S6†).

In conclusion, the fine nanorods of Cs_xWO_3 were successfully synthesized by the water controlled-release solvothermal process (WCRSP). From a practical application viewpoint, it is important to

realize high transmittance in the visible range together with excellent shielding of the NIR rays. The Cs_xWO_3 nanorods are a suitable functional material for solar filter applications (Fig. 4d). What is more, this original and novel method possesses great potential for the fabrication of other functional nanoparticles.

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