

Cyclic microwave synthesis and characterization of cadmium tungstate particles assisted by a solid-state metathetic reaction

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Cadmium tungstate (CdWO_4) particles synthesized using cyclic microwave irradiation assisted by a solid-state metathetic (SSM) reaction were well crystallized at 400-600 °C, showing a fine structure with a self-assembled rod-like morphology and a crystallographic orientation with sizes of 1-3 μm . The synthesized CdWO_4 particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. The optical properties were investigated by photoluminescence emission and Raman spectroscopy.

Key words: CdWO_4 , Cyclic microwave, Solid-state metathesis, Photoluminescence, Raman spectroscopy.

Introduction

Metal tungstates have attracted considerable attention for potential applications in photoluminescence, scintillator, photocatalyst and humidity sensors [1-3]. The physical, chemical and photochemical properties of metal tungstates are dependent on the manufacturing method. Several processes have been developed over the past decade to enhance the applications of metal tungstates prepared by a range of processes, such as co-precipitation [4, 5], a solvothermal method [5-8], spray pyrolysis [9], a reverse micelle system [10, 11], solution synthesis [12], a sol-gel method [13], a mechano-chemical method [14], a molten salt method [15, 16], a hydrothermal method [17-19], microwave-assisted synthesis [20-24] and a solid-state metathetic (SSM) reaction [25-27]. Wet chemical methods have disadvantages, such as complicated synthetic steps, use of expensive equipment, high synthetic temperatures and long sintering times.

Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, small particle size, narrow particle size distribution, and is a high purity method for preparing polycrystalline samples. Microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material via conduction. Microwave energy is delivered directly to the material through molecular interactions with an electromagnetic field. Heat can be generated through volumetric heating because microwaves can penetrate the material and supply

energy [23, 24]. Therefore it is possible to achieve rapid and uniform heating of thick materials. Solid-state synthesis of materials by the metathetic route is a simple and cost-effective method that provides a high yield with easy scale up, and is emerging as a viable alternative approach for the synthesis of high-quality novel inorganic materials in short time periods.

Therefore, the precise nature of the optical properties and microwave metathetic synthesis of cadmium tungstate (CdWO_4) particles is required for a wide range of applications. In this study, CdWO_4 particles were synthesized using a SSM method with microwave irradiation. The characteristics of the SSM reaction of the CdWO_4 particles are discussed in detail based on the formation of a high lattice energy by-product of NaCl. The synthesized CdWO_4 particles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties were examined by photoluminescence (PL) emission and Raman spectroscopy.

Experimental

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ of analytic reagent grade were used to prepare the CdWO_4 compound. Fig. 1 shows a flow chart for the cyclic microwave synthesis of CdWO_4 assisted by a metathetic reaction. The preparation of CdWO_4 was carried out by reacting well-ground mixtures of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ at a molar ratio of 1 : 1. The sample mixtures were dried at 100 °C for 12 h, placed into crucibles and exposed to domestic microwaves (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 40 minutes. The working cycle of the microwave oven was set between 60 s on and 30 s off. The samples were

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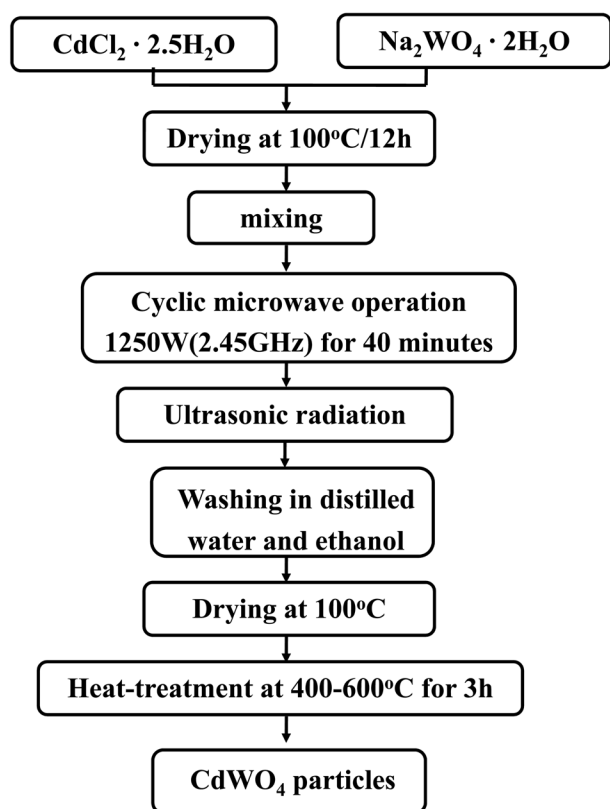


Fig. 1. Flow chart for the cyclic microwave synthesis of CdWO_4 assisted by a metathetic reaction.

treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove the sodium chloride reaction by-product. The samples were dried at 100 °C in an oven. Heat-treatments of the samples were performed at 400, 500 and 600 °C for 3 h.

The phase existing in the particles after the metathetic reactions and heat-treatment was identified by powder XRD ($\text{CuK}\alpha$, Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the thermal-decomposition behavior of the metathetic reaction and heat-treated particles over the frequency range, 400 to 4000 cm^{-1} . The microstructure and surface morphology of the CdWO_4 particles were observed by SEM (JSM-5600, JEOL, Japan). The microstructure of the rod-like morphology and the selected area electron diffraction (SAED) patterns were investigated using transmission electron microscopy (TEM, JEM 2000-FX, 250 kV, Japan). The PL spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using a LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as the excitation source, the power was kept at 0.5 mW on the sample.

Results and Discussion

Fig. 2 shows XRD patterns of the cyclic microwave synthesized CdWO_4 particles assisted by the metathetic

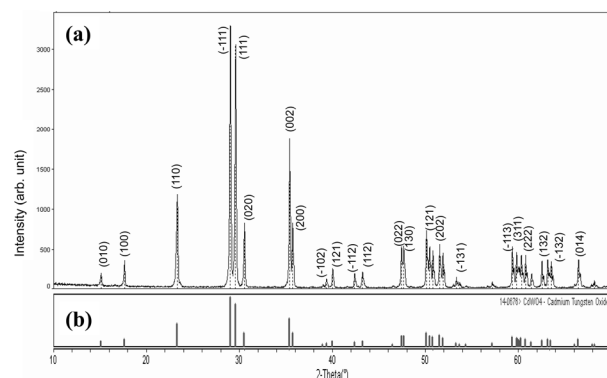


Fig. 2. XRD patterns of the cyclic microwave synthesized CdWO_4 particles assisted by the metathetic reaction after (a) heat-treatment at 600 °C for 3 h and compared to the (b) data of JCPDS 14-676.

reaction after (a) heat-treatment at 600 °C for 3 h and compared to the (b) data of JCPDS 14-676. All XRD peaks could be assigned to a tetragonal phase CdWO_4 with a monoclinic wolframite-type structure, which is in good agreement with the crystallographic data of CdWO_4 (JCPDS : 14-676). This means that the CdWO_4 can be prepared using this SSM reaction assisted by microwave irradiation. The formation of the CdWO_4 crystalline phases requires heat treatment at 600 °C for 3 h. The CdWO_4 formed had a wolframite-type crystal structure with lattice parameters of $a = 5.03 \text{ \AA}$ and $b = 5.86 \text{ \AA}$ and $c = 5.07 \text{ \AA}$ and $\beta = 91.47^\circ$ [18]. This suggests that solid-state metathetic synthesis is suitable for the growth of CdWO_4 crystallites and the development of the strongest intensity peaks at (110), (111) and (130) planes, which were the major peaks of the CdWO_4 , with some preferred orientation [7, 16, 18].

Fig. 3 shows SEM images of the CdWO_4 particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h, (c) 600 °C for 3 h and (d) a high magnification of (c). The SEM images after heat-treatment at 400 °C for 3 h

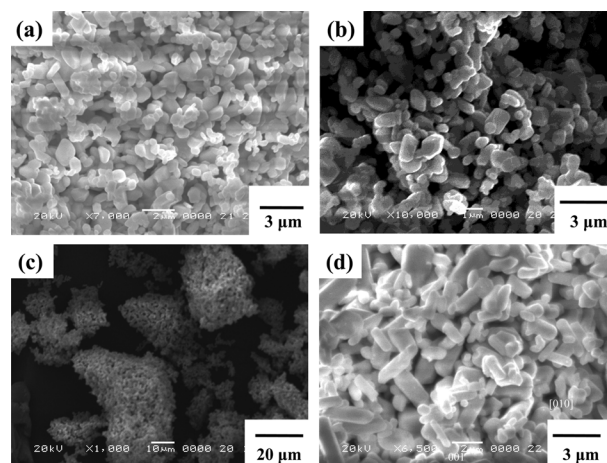


Fig. 3. SEM images of the CdWO_4 particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h, (c) 600 °C for 3 h and (d) a high magnification of (c).

in Fig. 3(a) and 500 °C for 3 h in Fig. 3(b) show silkworm-like morphologies with sizes of 1-2 μm . The SEM images after heat-treatment at 600 °C for 3 h show a woven network structure in Fig. 3(c) and various rod-like morphologies with sizes of 1-3 μm in Fig. 3(d).

Fig. 4 shows (a) TEM image after heat-treatment at 600 °C for 3 h and (b) a SAED of a various rod-like assembly, (c) a schematic illustrations of the self-assembled rod-like morphology and (d) various rod-like morphology of CdWO_4 . The TEM image in Fig. 4(a) shows a self-assembled rod-like morphology and the SAED pattern in Fig. 4(b), which can be indexed to the [010] zone, shows the preferred growth direction of these rods. The CdWO_4 easily forms relatively thin structures due to its intrinsic (010) cleavage plane because of the chain structure of the $[\text{WO}_6]^{6-}$ octahedra in the wolframite type structure. The self-assembled rod-like and various short rod-like morphologies of CdWO_4 are constructed with several submicrometre-rods attached in their arrangements in Fig. 4(c, d). It is noted that most of the assembled rods have similar widths. The reason why the rod-like morphology is formed in CdWO_4 is attributed to the crystallographic growth of the CdWO_4 particles which can be generated easily in the direction [100], while the assembled structures can be attached to the direction [001] as in Fig. 4(d). A similar self-assembled structure on the CdWO_4 short nanorods and nanofibers [18] shows a relatively thick nature along the [010] direction and self-assembles to an ordered structure with (001) and (010) faces, while the nanorods are flexible and vertically self-assembled to form a woven network. It is assumed that CdWO_4 has the (010) cleavage plane and weakly bound to (100) and (001) planes. The surface energy of the (010) plane can be easily lowered relative to that of (100) and (001) planes. The CdWO_4 structures are constructed by self-assembled rod-like and various short rod-like morphologies attaching to their (001) and (010) planes. Based on the result of SAED of CdWO_4 short nanorods [18], the preferred growth direction of the rods is [100] and has a relative thick nature along [001]. Therefore, the

crystallographic growth can be generated easily in the direction [100] in Fig. 4(c) and (d).

The sample mixtures of CdCl_2 and Na_2WO_4 were heated by a microwave-assisted solid-state metathetic route. The microwave metathetic synthesis of various metal tungstates and molybdates [25, 26] provides the exothermic energy to synthesize metal tungstates and molybdates. It helped to heat the bulk of the material uniformly resulting in fine particles with a controlled morphology, and to fabricate the product in a green manner without the generation of solvent waste. Solid state metathetic reactions, such as $\text{CdCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{CdWO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, where the driving force is the exothermic reaction accompanying the formation of NaCl with a high lattice energy [23, 24]. SSM reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The solid-state metathesis reactions provide a convenient route for the synthesis of CdWO_4 , which were obtained in the form of loosely connected submicrometre sized particles at considerably lower temperatures than those usually employed for their synthesis. After the microwave metathetic reaction, the reactants need to be heated at temperatures at 400, 500, 600 °C for 3 h. Generally, the solid state reaction to synthesize CdWO_4 requires to heat up to temperatures above 900 °C for 12 h. Therefore, the microwave metathetic reaction and post-heat treatment are interdependently essential procedures to synthesize CdWO_4 at a lower temperature than that employed for solid state reactions. Wet chemical methods for the synthesis of tungstates require low temperatures [10-13]. However, the solution methods need complicated synthetic steps, the use of expensive equipment and produce a small amount of CdWO_4 products. Compared with the usual methods, microwave synthesis has the advantages of a very short reaction time, a small particle size, a narrow particle size distribution, and is a high purity method for preparing CdWO_4 particles. It is possible to achieve rapid and uniform heating of CdWO_4 by the solid-state synthesis of materials by the metathetic route which is a simple and cost-effective method that provides a high yield with easy scale up, and is emerging as a viable alternative approach for the synthesis of CdWO_4 particles in short time periods.

Metal tungstates with large bivalent cations (e.g., Ca, Ba, Pb, and Sr) tend to have a scheelite-type tetragonal structure, whereas small cationic radii (e.g., Zn, Fe, Co, Ni and Cd) favor the formation of a wolframite-type monoclinic structure. The main difference between the above two structures is that each W atom is surrounded by four O atoms in a scheelite-type structure, whereas the wolframite-type structure contains six O atoms surrounding each W atom [28, 29]. It is based on a distorted hexagonal close packing of O atoms with Cd and W atoms, each occupying one-fourth of the octahedral interstices. The presence of two non-equivalent oxygen atoms is responsible for the pairs of Cd-O and W-O bonds with different lengths. Therefore, both Cd and W atoms are surrounded by six oxygen atoms, forming distorted octahedral coordination.

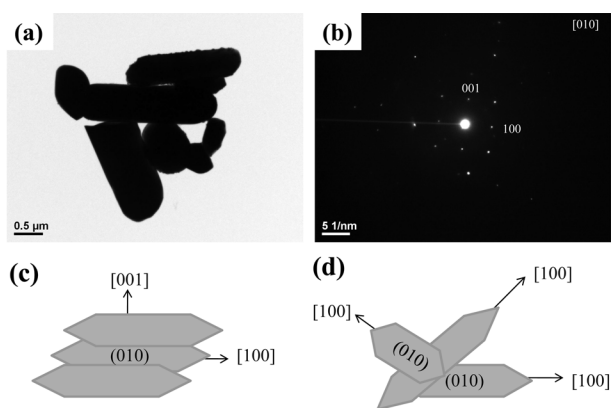


Fig. 4. A (a) TEM image after heat-treatment at 600 °C for 3 h and (b) SAED of a various rod-like assembly, (c) schematic illustrations of the self-assembled rod-like morphology and (d) various rod-like morphology of CdWO_4 .

Each chain of the CdO_6 octahedra is corner-linked, and the chains of WO_6 octahedra are edge-linked, which are also parallel to [001]. The CdO_6 and WO_6 octahedra consist of three pairs of cation-oxygen bonds with Cd and W atoms being displaced from the center of their octahedra by approximately 0.29 and 0.32 Å, respectively, along the [010] direction [30].

Fig. 5 shows FT-IR spectra at the wavenumber range of 480–4000 cm^{-1} of the CdWO_4 particles after (a) the microwave metathetic reaction ($\text{CdWO}_4\text{-m}$) and (b) heat-treatment at 600 °C for 3 h ($\text{CdWO}_4\text{-m600}$). The bending and stretching vibrations of Cd-O (532 cm^{-1}), W-O (629, 691 cm^{-1}) and Cd-O-W (833, 878 cm^{-1}) were identified in the synthesized CdWO_4 . The FT-IR spectra of the $\text{CdWO}_4\text{-m}$ in Fig. 5(a) exhibit bands at 1620, 3445 cm^{-1} (O-H stretching modes) at 1278 cm^{-1} (CH_3). It is assumed

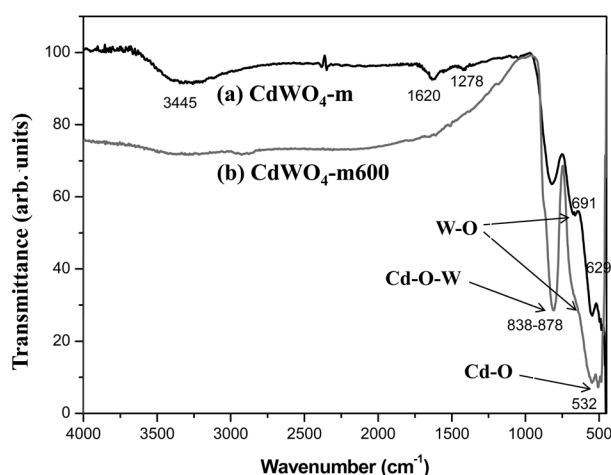


Fig. 5. FT-IR spectra of the CdWO_4 particles after (a) the microwave metathetic reaction ($\text{CdWO}_4\text{-m}$) and (b) heat-treatment at 600 °C for 3 h ($\text{CdWO}_4\text{-m600}$).

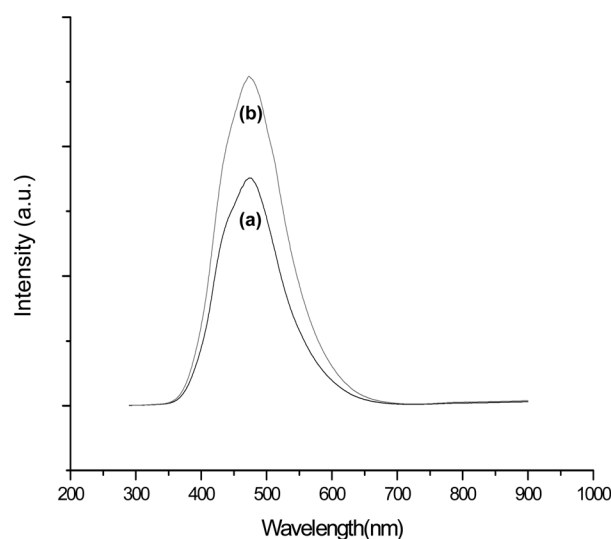


Fig. 6. Photoluminescence emission spectra of the CdWO_4 particles after heat-treatment at (a) 500 °C for 3 h and (b) 600 °C for 3 h excited by 250 nm source at room temperature.

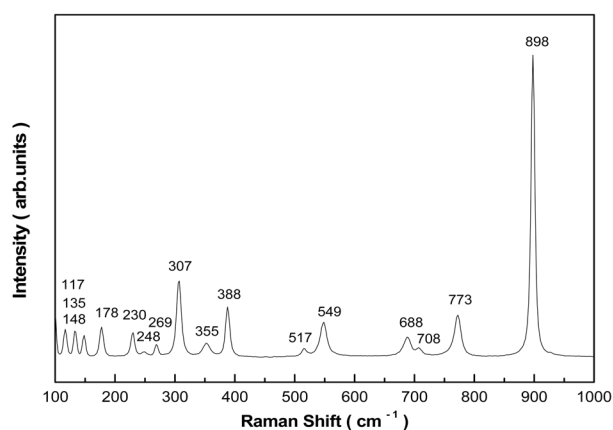


Fig. 7. Raman spectra of the CdWO_4 particles after heat-treatment at 600 °C for 3 h excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample.

that the samples prepared contain a significant amount of surface-adsorbed water and alcohol. Obviously, the bands at 1620, 3445, 1278 cm^{-1} disappeared after heat-treatment at 600 °C for 3 h in Fig. 5(b).

Fig. 6 presents photoluminescence emission spectra of the CdWO_4 particles after heat-treatment at (a) 500 °C for 3 h and (b) 600 °C for 3 h excited by a 250 nm source at room temperature. The photoluminescence of metal tungstates has been discussed in the frame of molecular orbital models of the $[\text{WO}_6]^{6-}$ group. It is generally assumed that the measured emission spectra of metal tungstates are mainly attributed to the charge-transfer transitions within the $[\text{WO}_6]^{6-}$ complex [31–33]. With excitation at 250 nm, the CdWO_4 particles exhibit a broad PL emission in the green wavelength range of 460–470 nm, which agrees with the PL emission of a CdWO_4 single crystal at room temperature what has been reported which intrinsic luminescence at 470–480 nm [34, 35]. The photoluminescence intensity of energy-conversion materials depends strongly on the particle shape and distribution. Generally, for samples with a similar morphologies, a homogenized particle must be favorable to luminescent characteristics because of less contamination or fewer dead layers on the energy-conversion materials surface.

Fig. 7 shows Raman spectra of the CdWO_4 particle excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the sample. The vibration modes in the Raman spectra of tungstates are classified into two groups, internal and external [36, 37]. The internal vibrations can be explained by the $[\text{WO}_6]^{6-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Cd^{2+} cation and rigid molecular units. The internal Raman modes for the CdWO_4 particles in Fig. 7 were detected at 898, 773, 688, 549, 388 and 307 cm^{-1} . The well-resolved sharp peaks for the CdWO_4 particles indicate that the synthesized particles are highly crystallized. The free rotation modes were detected at 248, 230 cm^{-1} and the external modes were localized at 178–117 cm^{-1} .

Conclusions

Cadmium tungstate (CdWO_4) particles synthesized using a cyclic microwave metathetic reaction were well crystallized at 400-600 °C. Silkworm-like morphologies were formed after heat-treatment at 400-500 °C for 3 h with sizes of 1-2 μm , while a self-assembled rod-like morphology with a preferred crystallographic orientation with sizes of 1-3 μm was formed after 600 °C for 3 h. A stretching vibration in FTIR was detected as a strong W-O stretch in the $[\text{WO}_6]^{6-}$ tetrahedra at 823 cm^{-1} . With excitation at 250 nm, the CdWO_4 particles exhibit a broad PL emission in the green wavelength range of 460-470 nm. The well-resolved Raman spectra for the CdWO_4 particles at 898, 773, 688, 549, 388 and 307 cm^{-1} provide evidence of the highly crystallized structure. Free rotation modes were detected at 248, 230 cm^{-1} and the external modes were localized at 178-117 cm^{-1} .

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