



Microwave-Assisted Synthesis and Photoluminescence of CdWO₄ by A Solid-State Metathetic Route†

CHANG SUNG LIM

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, South Korea

Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

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Cadmium tungstate (CdWO₄) particles were synthesized using a solid-state metathetic (SSM) route assisted by cyclic microwave irradiation. The CdWO₄ particles 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 CdWO₄ 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: CdWO₄, Cyclic microwave, Solid-state metathesis, Photoluminescence, Raman spectroscopy.

INTRODUCTION

Metal tungstates have attracted considerable attention for potential applications in photoluminescence, scintillator, photocatalyst and humidity sensors¹⁻³. 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 method⁶⁻⁸, spray pyrolysis⁹, a reverse micelle system^{10,11}, solution synthesis¹², a sol-gel method¹³, a mechano-chemical method¹⁴, a molten salt method^{15,16}, a hydrothermal method¹⁷⁻¹⁹, microwave-assisted synthesis²⁰⁻²⁴ and a solid-state metathetic (SSM) reaction²⁵⁻²⁷. 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. Microwave assisted SSM synthesis of materials by the metathetic route is a simple and cost-effective method that provides a high yield with easy to 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 by microwave-assisted SSM synthesis of CdWO₄ particles is required for a wide range of applications. In this study, CdWO₄ particles were synthesized using a SSM method with microwave irradiation. The characteristics of the SSM reaction of the CdWO₄ particles are discussed based on the formation of a high lattice energy by-product of NaCl. The synthesized CdWO₄ particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and transmission electron microscopy. The optical properties were examined by photoluminescence emission and Raman spectroscopy.

EXPERIMENTAL

CdCl₂·2.5H₂O and Na₂WO₄·2H₂O of analytic reagent grade were used to prepare the CdWO₄ compound. The preparation of CdWO₄ was carried out by reacting well-ground mixtures of CdCl₂·2.5H₂O and Na₂WO₄·2H₂O 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

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(Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 40 min. The working cycle of the microwave oven was set between 60 s on and 30 s off. The samples were 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 existings in the particles after the metathetic reactions and heat-treatment was identified by powder XRD (CuK α , Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the thermal-decomposition behaviour of the metathetic reaction and heat-treated particles over the frequency range, 4000-400 cm⁻¹. The microstructure and surface morphology of the CdWO₄ particles were observed by SEM (JSM-5600, JEOL, Japan). The microstructure of the rod-like morphology and selected area electron diffraction (SAED) patterns were investigated using transmission electron microscopy (TEM, JEM 2000-FX, 250 kV, Japan). The photoluminescence 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. 1 shows XRD patterns of the cyclic microwave synthesized CdWO₄ particles assisted by a metathetic reaction followed by further (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 CdWO₄ with a monoclinic wolframite-type structure, which is in good agreement with the crystallographic data of CdWO₄ (JCPDS: 14-676). This means that the CdWO₄ can be prepared using this SSM reaction assisted by microwave irradiation. The formation of the CdWO₄ crystalline phases requires heat treatment at 600 °C for 3 h. The CdWO₄ 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 SSM synthesis is suitable for the growth of CdWO₄ crystallites and the development of the strongest intensity peaks at (110), (111) and (130) planes, which were the major peaks of the CdWO₄, with some preferred orientation^{7,16,18}.

Fig. 2 shows SEM images of the CdWO₄ 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 in Fig. 2(a) and 500 °C for 3 h in Fig. 2(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. 2(c) and various rod-like morphologies with sizes of 1-3 μm in Fig. 2(d).

Fig. 3 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 CdWO₄. The TEM image in Fig. 3(a) shows a self-assembled rod-like morphology

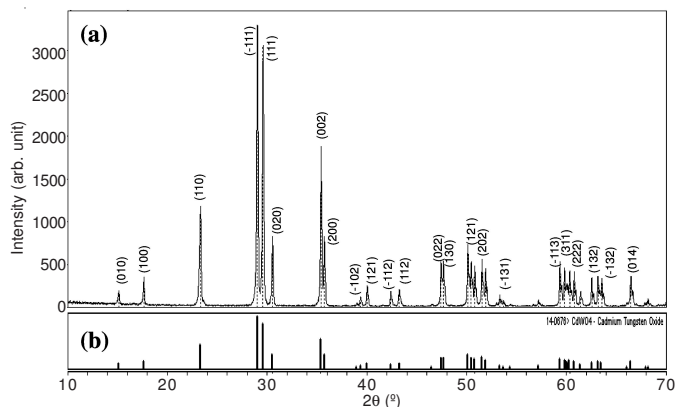
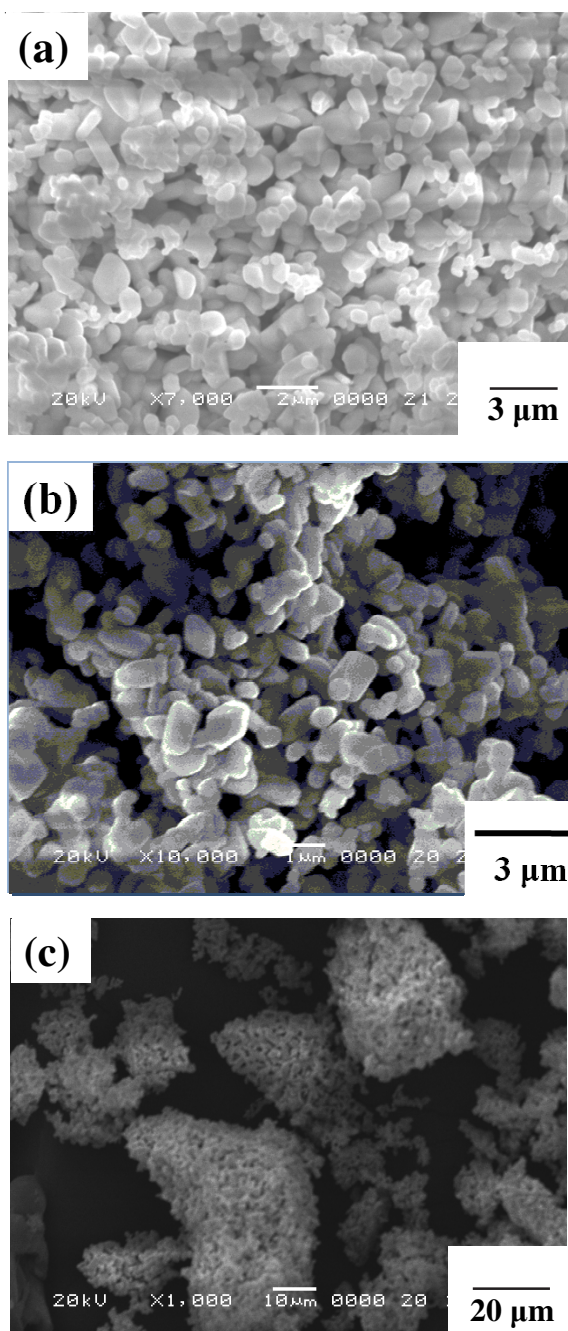


Fig. 1. XRD patterns of the cyclic microwave synthesized CdWO₄ particles assisted by a metathetic reaction followed by further (a) heat-treatment at 600 °C for 3 h and compared to the (b) data of JCPDS 14-676



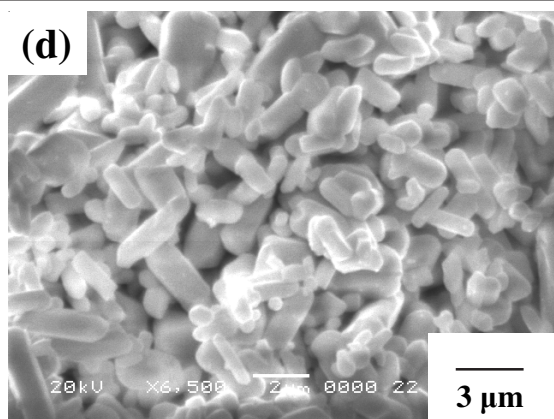


Fig. 2. SEM images of the CdWO₄ particles after heat-treatment at (a) 400 °C for 3 h, (b) 500 °C for 3 h, (c) 600 °C for 3 h and (d) a high magnification of (c)

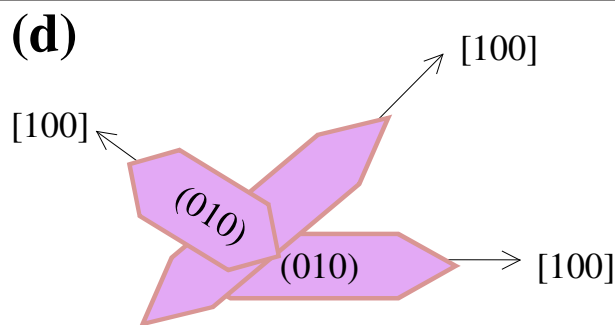
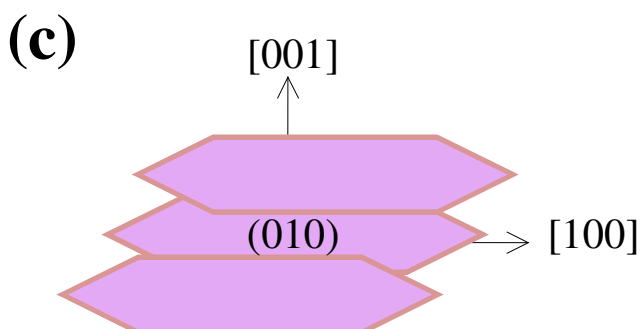
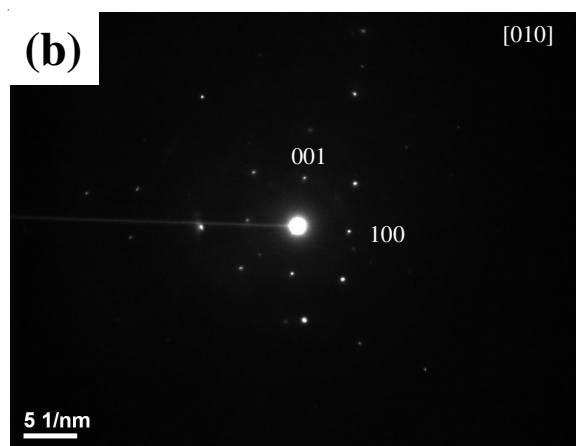
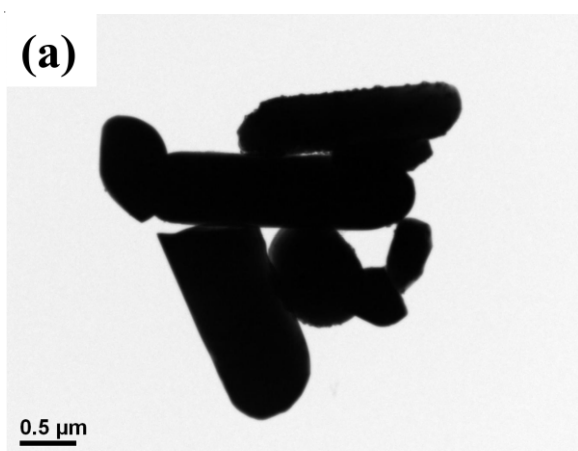


Fig. 3. A (a) TEM image after heat-treatment at 600 °C for 3 h and (b) SAED of a various rod-like assembly, (c) schematic illustrations of the self-assembled rod-like morphology and (d) various rod-like morphology of CdWO₄

and the SAED pattern in Fig. 3(b), which can be indexed to the [010] zone, shows the preferred growth direction of these rods. The CdWO₄ easily forms relatively thin structures due to its intrinsic (010) cleavage plane because of the chain structure of the [WO₆]⁶⁻ octahedra in the wolframite type structure. The self-assembled rod-like and various short rod-like morphologies of CdWO₄ are constructed with several submicrometer-rods attached in their arrangements in Fig. 3(c, d). It is noted that most of the assembled rods have similar widths. The reason why the rod-like morphology are formed in CdWO₄ is attributed to the crystallographic growth of the CdWO₄ particles which can be generated easily in the direction [100], while the assembled structures can be attached to the direction [001] as in Fig. 3(d). A similar self-assembled structure on the CdWO₄ short nanorods and nanofibers¹⁸ 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 CdWO₄ 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 CdWO₄ 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 CdWO₄ short nanorods¹⁸, 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. 3(c-d).

The sample mixtures of CdCl₂ and Na₂WO₄ were heated by a microwave-assisted SSM 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 fabricate the product in a green manner without the generation of solvent waste. SSM reactions, such as CdCl₂ + Na₂WO₄ → CdWO₄ + 2NaCl, 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}. Solid-state metathetic reactions occur so rapidly that the exothermic reaction is essentially used to heat up the solid products. The SSM reactions provide a convenient route for the synthesis of CdWO₄, which were obtained in the form of loosely connected submicrometer 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 and 600 °C for 3 h. Generally, the solid state reaction to synthesize CdWO₄ requires to heat up to the temperatures above 900 °C for 12 h. Therefore, the microwave SSM reaction and post-heat treatment are interdependently essential procedures to synthesize CdWO₄ at a lower temperature than that employed for solid state reactions. Wet chemical methods for the synthesis of tungstates require low temperatures¹⁰⁻¹³. However, the solution methods need complicated synthetic steps, the use of expensive equipment and produce a small amount of CdWO₄ 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 CdWO₄ particles. It is possible to achieve rapid and uniform heating of CdWO₄ 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 to scale up and is emerging as a viable alternative approach for the synthesis of CdWO₄ 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) favour 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. Each chain of the CdO₆ octahedra is corner-linked and the chains of WO₆ octahedra are edge-linked, which are also parallel to [001]. The CdO₆ and WO₆ 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] direction³⁰.

Fig. 4 shows FT-IR spectra at the wavenumber range of 4000-480 cm⁻¹ of the CdWO₄ particles after (a) the microwave metathetic reaction (CdWO₄-m) and (b) heat-treatment at 600 °C for 3 h (CdWO₄-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 CdWO₄. The FT-IR spectra of the CdWO₄-m in Fig. 4(a) exhibit bands at 3445, 1620 cm⁻¹ (O-H stretching modes) at 1278 cm⁻¹ (CH₃). It is assumed that the samples prepared contain a significant amount of surface-adsorbed water and alcohol. Obviously, the bands at 3445, 1620, 1278 cm⁻¹ disappeared after heat-treatment at 600 °C for 3 h in Fig. 4(b).

Fig. 5 presents photoluminescence emission spectra of the CdWO₄ 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 [WO₆]⁶⁻ group. It is generally assumed that the measured emission spectra of metal tungstates are mainly attributed to the charge-transfer transitions within the [WO₆]⁶⁻ complex³¹⁻³³.

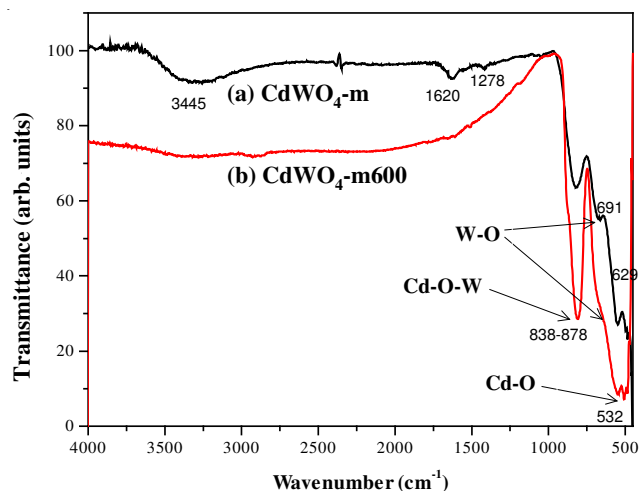


Fig. 4. FT-IR spectra of the CdWO₄ particles after (a) the microwave metathetic reaction (CdWO₄-m) and (b) heat-treatment at 600 °C for 3 h (CdWO₄-m600)

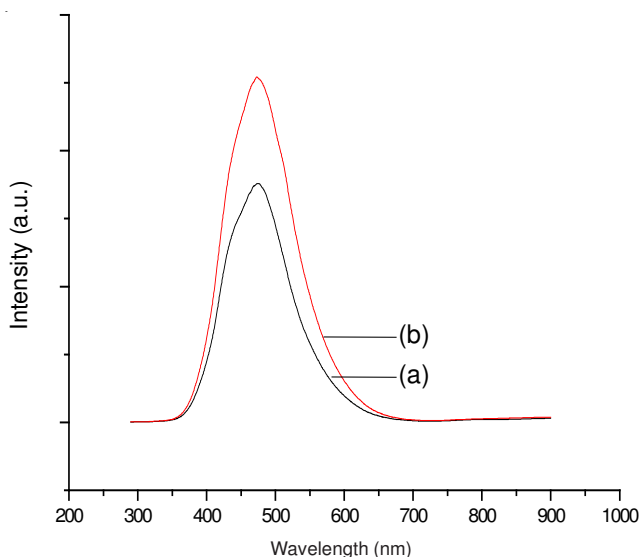


Fig. 5. Photoluminescence emission spectra of the CdWO₄ particles after heat-treatment at (a) 500 °C for 3 h and (b) 600 °C for 3 h excited by 250 nm source at room temperature

With excitation at 250 nm, the CdWO₄ particles exhibit a broad photoluminescence emission in the green wavelength range of 460-470 nm, which agrees with the photoluminescence emission of a CdWO₄ single crystal at room temperature what has been reported with 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 morphology, a homogenized particle must be favorable to luminescent characteristics because of less contamination or fewer dead layers on the energy-conversion materials surface.

Fig. 6 shows Raman spectra of the CdWO₄ particle excited by a 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 [WO₆]⁶⁻ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Cd²⁺ cation and rigid molecular units. The internal

Raman modes for the CdWO_4 particles in Fig. 6 were detected at 898, 773, 688, 549, 388 and 307 cm^{-1} . The free rotation modes were detected at 248, 230 cm^{-1} and the external modes were localized at 178-117 cm^{-1} . The internal Raman modes for the CdWO_4 particles in Fig. 6 were detected at 898, 773, 688, 549, 388 and 307 cm^{-1} . The free rotation modes were detected at 248, 230 cm^{-1} and the external modes were localized at 178-117 cm^{-1} . The well-resolved sharp peaks for the CdWO_4 particles indicate that the synthesized particles are highly crystallized.

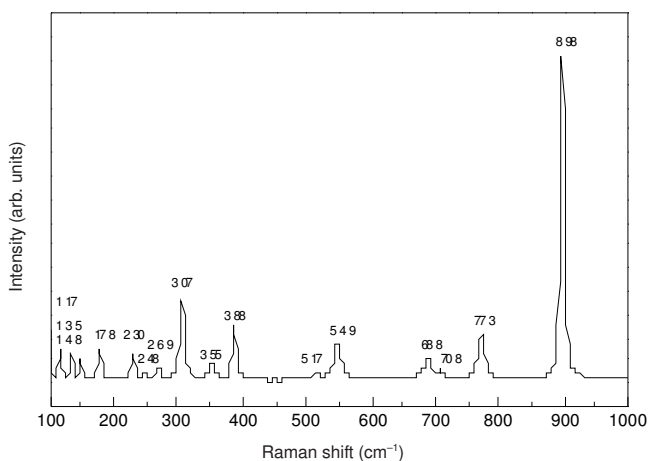


Fig. 6. Raman spectra of the CdWO_4 particles after heat-treatment at 600 $^{\circ}\text{C}$ for 3 h excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

Conclusion

CdWO_4 particles synthesized using a cyclic microwave metathetic reaction were well crystallized at 400-600 $^{\circ}\text{C}$. Silk-worm-like morphologies were formed after heat-treatment at 400-500 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ 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 photoluminescence emission in the green wavelength range of 460-470 nm. The internal Raman modes for the CdWO_4 particles in Fig. 6 were detected at 898, 773, 688, 549, 388 and 307 cm^{-1} . Free rotation modes were detected at 248, 230 cm^{-1} and the external modes were localized at 178-117 cm^{-1} . The well-resolved sharp peaks for the CdWO_4 particles indicate that the synthesized particles are highly crystallized.

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