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Preparation and Characterization of Strontium Orthovanadate Nanoparticles by A Microwave-Assisted Solvothermal Method

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Strontium orthovanadate ($Sr_3V_2O_8$) nanoparticles were synthesized successfully using a facile microwave solvothermal route followed by further heat-treatment. Well-crystallized $Sr_3V_2O_8$ nanoparticles were formed after heat-treatment at 600 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 100-150 nm. The synthesized $Sr_3V_2O_8$ nanoparticles 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: Strontium orthovanadate, Microwave-assisted solvothermal synthesis, Nanoparticles, Luminescence, Raman spectroscopy.

INTRODUCTION

White light-emitting diode (LED) have been attracted as a successor of a new light source to the fluorescence and incandescent lamps. The white light-emitting diode was mainly consisted of blue LED and yellow-red phosphors or ultraviolet LED and blue-green-red phosphors. Many inorganic or organic phosphors have already found for these white LED. Among various number of phosphors, metal orthovanadates have attracted considerable attention for potential applications in the broadband photoluminescence in the visible light range, as well as IR-laser, photocatalyst, ferroelectric and microwave devices[1-3]. The broadband emission in the visible light range is effective to obtain a good colour rending property for the lighting devices. In recent years, the fabrication processes of metal orthovanadates have been developed to enhance the applications of metal orthovanadate prepared by a range of processes, such as a solid-state reaction[4,5], a solution phase metathetic method[6], sol-gel[7], a solid-state metathesis approach[8], a mechano-chemical method[9] and a floating zone technique[10]. Hydrothermal process is an efficient low temperature method that allows the formation of particles with high degree of crystallinity and easy dispersion in an aqueous medium. Microwave energy is delivered directly to the material through molecular interactions with an electromagnetic field[11]. The use of microwave energy in hydrothermal system promotes the development of a rapid heating to the required temperature with rapid rates of crystallization[12,13]. Recently, microwave solvothermal processes have been reported the use of a facile and fast method in preparing nanocrystalline particles of metal tungstates with unique and enhanced properties by a microwave solvothermal process[14,15].

Solvothermal process is one of the most powerful method employed for the crystallization of various unique nanoparticles. The solvothermal synthesis proceeds the reaction in a hot ethylene glycol solution as a polar solvent with a boiling point of 197 ºC. When the microwave radiation is supplied to the ethylene glycol under a sealed pressure above boiling point, the components dissolving in the ethylene glycol are charged and vibrated in electric field interdependently. The microwave solvothermal process is adjusted to heat the $Sr_3V_2O_8$ uniformly resulting in fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste.

In the present study, the $Sr_3V_2O_8$ nanoparticles were synthesized using a facile solvothermal route assisted by the microwave irradiation. The characteristics of the synthesized $Sr_3V_2O_8$ nanoparticles are discussed in detail based on the microwave solvothermal reaction in ethylene glycol under the high sealed pressure. The synthesized $Sr_3V_2O_8$ nanoparticles 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

Fig. 1 shows a flow chart for the synthesis of $Sr_3V_2O_8$ nanoparticles by the microwave solvothermal process. $SrCl_2{\cdot}6H_2O$, Na_3VO_4 and ethylene glycol of analytic reagent grade were used to prepare the $Sr_3V_2O_8$ compound. Each of 0.012 mol $SrCl_2{\cdot}6H_2O$ and 0.008 mol Na_3VO_4 was dissolved in 30 mL ethylene glycol. The solutions were mixed and adjusted at a pH 9.5 using NaOH. The aqueous solution was stirred in ultrasonic bath at room temperature. In the sequence, the mixture was transferred into a Teflon lined digestion vessel of 120 mL capacity. The Teflon vessel was placed into a microwave solvothermal autoclave (2.45 GHz, maximum power of 800 W). The microwave solvothermal conditions were kept at 200 ºC for 0.5 h. After microwave solvothermal process, the microwave autoclave was cooled room temperature. The resulting solutions were treated with ultrasonic radiation and washed many times with distilled hot water. The white precipitates were corrected and dried at 100 ºC in a dry oven. The final products were heat-treated at 600 ºC for 3 h.

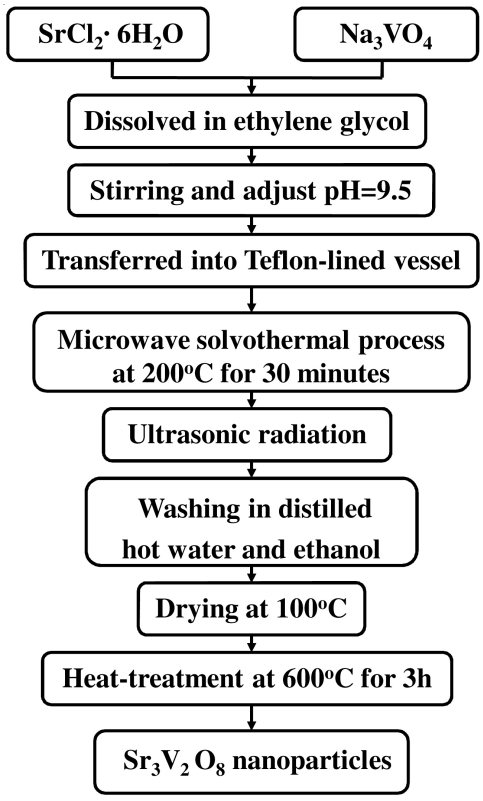

Fig. 1. Flow chart for the synthesis of $Sr_3V_2O_8$ nanoparticles by the microwave solvothermal process

The existing phases of the $Sr_3V_2O_8$ particles after the microwave solvothermal process were identified by powder XRD (CuK_α, Rigaku D/MAX 2200, Japan). FTIR (Nicolet IR 200, Thermo Electron Corporation, USA) was used to examine the absorption behaviour of the synthesized $Sr_3V_2O_8$ particles over the frequency range, 4000-400 cm^{-1}. The microstructure, particle morphology and qualitative compositions of the $Sr_3V_2O_8$ particles were observed by SEM (JSM-5600, JEOL, Japan) and 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 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 samples.

RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the $Sr_3V_2O_8$ nanoparticles synthesized by the microwave solvothermal process after heat-treatment at 600 ºC for 3 h. All observed diffraction peaks could be assigned to the trigonal phase (space group R-3m), which is in good agreement with the crystallographic data of $Sr_3V_2O_8$ (JCPDS: 81-1844)[8]. This means that the trigonal phases of $Sr_3V_2O_8$ can be prepared using this solvothermal process assisted by a cyclic microwave irradiation. It suggests that microwave solvothermal synthesis is suitable for the growth of $Sr_3V_2O_8$ crystallites and development of the strongest intensity peaks from the (015), (110) and (205) planes, which were the major peaks of the $Sr_3V_2O_8$, with some preferred orientation. The small amount of NaCl marked with # at 13.2º was observed. The microwave solvothermal process occurs in accordance with the reaction:

$$3SrCl_2{\cdot}6H_2O + 2Na_3VO_4 \rightarrow Sr_3V_2O_8 + 6NaCl + 18H_2O$$

The presence of the residual NaCl was resulted from this solvothermal reaction.

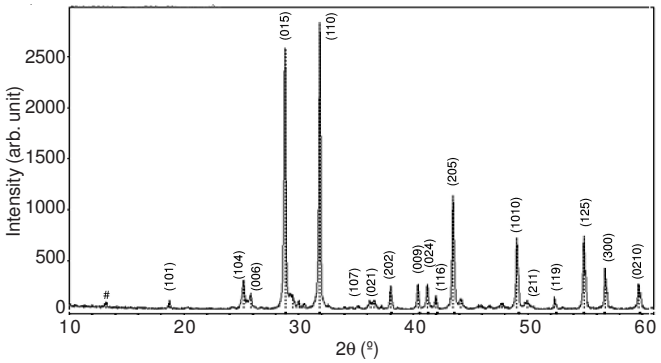

Fig. 2. XRD patterns of the $Sr_3V_2O_8$ nanoparticles synthesized

Fig. 3 shows a SEM image (a) and a TEM image (b) of the $Sr_3V_2O_8$ nanoparticles synthesized by the microwave solvothermal process. The SEM image of $Sr_3V_2O_8$ in Fig. 3(a) shows a well-defined and homogeneous morphology, while the TEM image of $Sr_3V_2O_8$ in Fig. 3(b) shows the particle sizes of 100-150 nm. The solvothermal synthesis proceeds the reaction of $SrCl_2{\cdot}6H_2O$ + Na_3VO_4 in a hot ethylene glycol solution as a polar solvent with a boiling point of 197 ºC. When the microwave radiation is supplied to the ethylene glycol under a sealed pressure above boiling point, the components dissolving in the ethylene glycol are charged and vibrated in electric field interdependently. The microwave solvothermal process is adjusted to heat the metal orthovanadates uniformly resulting in fine particles with a controlled morphology and to fabricate the product in a green manner without the generation of solvent waste. The microwave-assisted solvothermal reaction involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction in ethylene glycol accompanying the formation of NaCl with a high lattice energy.

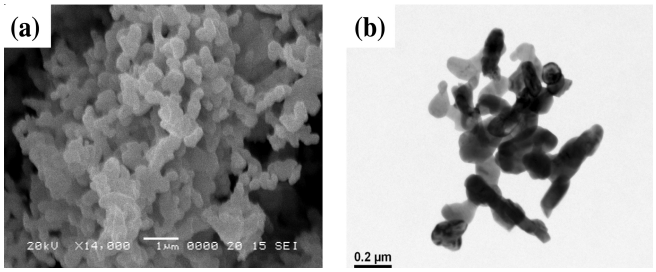

Fig. 3. SEM image (a) and TEM image (b) of the $Sr_3V_2O_8$ nanoparticles

The microwave exothermic reaction occurs so rapidly that the temperature and the pressure of the ethylene glycol increases so quickly that the reaction products are essentially heated up. The microwave-assisted solvothermal reactions provide a facile route for the synthesis of $Sr_3V_2O_8$ nanoparticles, which were obtained in the form of loosely connected nano-sized particles at considerably lower temperatures with a high pressure than those usually employed for their synthesis. The well-defined $Sr_3V_2O_8$ nanoparticle features synthesized by the microwave-assisted solvothermal process have a control over the morphology of the final particles and can be used for technological applications.

Fig. 4 shows FT-IR spectrum of the $Sr_3V_2O_8$ nanoparticles synthesized by the microwave solvothermal process in the wavenumber range, 4000-480 cm^{-1}. The large isolated absorbable peak around 820 cm^{-1} reveals typical characteristic of a strong V-O stretching in the $[VO_4]^{3-}$ with a strong IR absorbable band at 920 cm^{-1}. The strong V-O stretching peaks are contributed to the uniform regular $[VO_4]^{3-}$ tetrahedron of the metal orthovanadates. Fig. 5 shows photoluminescence emission spectrum of the synthesized $Sr_3V_2O_8$ nanoparticles exited at 250 nm at room temperature. The emission spectra of metal orthovanadates are due mainly to charge-transfer transitions within the $[VO_4]^{3-}$ complex. With excitation at 250 nm $Sr_3V_2O_8$ nanoparticles exhibit major photoluminescence emissions in the blue wavelength range of 420-430 nm. The spectrum shows broad peaks on which is superimposed considerable several fine structures.

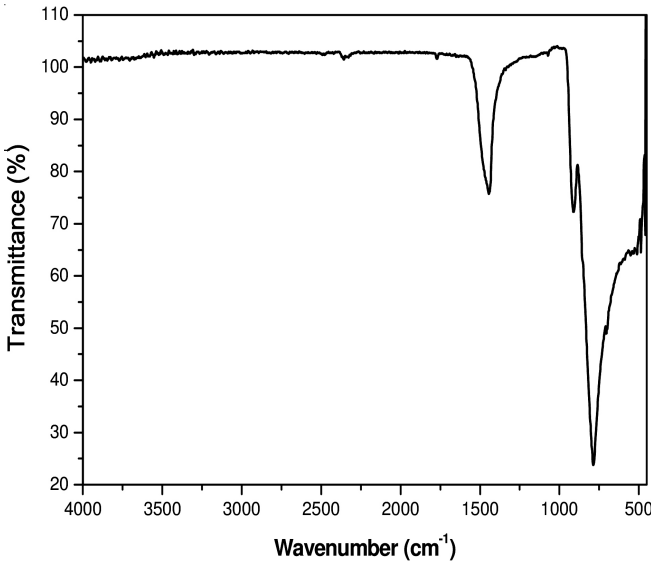

Fig. 4. FT-IR spectrum of the $Sr_3V_2O_8$ nanoparticles synthesized

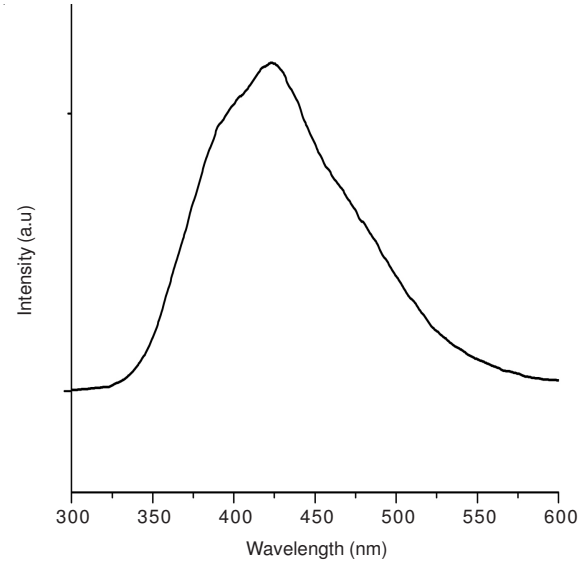

Fig. 5. Photoluminescence emission spectrum of the synthesized $Sr_3V_2O_8$ nanoparticles exited at 250 nm at room temperature

Fig. 6 shows Raman spectrum of the $Sr_3V_2O_8$ nanoparticles excited by the 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on the samples. The vibration modes in the Raman spectra of $Sr_3V_2O_8$ nanoparticles are classified into two groups, internal and external. The internal vibrations are related to the $[VO_4]^{3-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Sr^{2+} cation and rigid molecular units. The Raman modes for the $Sr_3V_2O_8$ nanoparticles were detected as $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 860, 855, 785, 396 and 329 cm^{-1}, respectively. The free rotation mode was detected at 180 cm^{-1} and the external modes were localized at 146 and 127 cm^{-1}. The well-resolved sharp peaks for the $Sr_3V_2O_8$ nanoparticles indicate that the synthesized particles are highly crystallized.

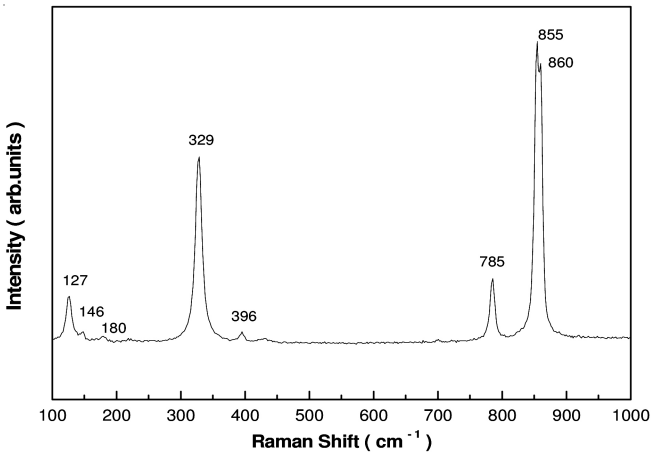

Fig. 6. Raman spectrum of the synthesized $Sr_3V_2O_8$ nanoparticles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the samples

Conclusion

Strontium orthovanadate ($Sr_3V_2O_8$) nanoparticles were synthesized successfully using a facile microwave solvothermal route in a hot ethylene glycol solution as a polar solvent. Well-

crystallized $Sr_3V_2O_8$ nanoparticles were formed after heat-treatment at 600 ºC for 3 h showing a fine and homogeneous morphology with particle sizes of 100-150 nm. With excitation at 250 nm, the $Sr_3V_2O_8$ exhibit major photoluminescence emissions in the blue wavelength range of 420-430 nm. The Raman modes for the $Sr_3V_2O_8$ nanoparticles were detected at 860, 855, 785, 396 and 329 cm^{-1}, the free rotation mode was detected at 180 cm^{-1} and the external modes were localized at 146 and 127 cm^{-1}. The well-resolved sharp peaks for the $Sr_3V_2O_8$ nanoparticles indicate that the synthesized particles are highly crystallized.

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