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Luminescence property of aqueous reaction-derived $MnWO_4$ powder and electrophoretic deposited thin film

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Hubnerite $MnWO_4$ powders have been synthesized by aqueous reaction. The $MnWO_4$ films were deposited on p-Si substrate with an electrophoretic process. The powders and film were characterized by X-Ray diffractometion (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence spectral analysis. Single phase $MnWO_4$ powders with monoclinic hubnerite structure can be directly formed from the aqueous solutions at room temperature. TEM micrograph indicated that powders had uniform rodlike morphology with particle size about 32 nm. The powders exhibited a broad blue-green emission band centered at 462.7 nm (2.68 eV). The calcining at 400 ℃ obviously enhanced the excitation and emission, while the lattice parameter decreases and the surface smoothness increases. The film deposited on the cathode was more homogeneous continues compared to the films deposited on anode. The intensities in luminescence of the films were about one half of the powder.

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Keywords: $MnWO_4$, Powders, Film, Electrophoretic deposition, Luminescence

1. Introduction

$MnWO_4$ nanopowders have been widely studied as antiferrimagnetic materials [1-3], humidity sensors [4-7], ferroelectric materials [8-10]. Luminescence materials have widely potential applications in agriculture, industry and medicine and pharmacology. However, luminescent properties of $MnWO_4$ nanocrystal have not been reported previously. Manganous tungstate ($MnWO_4$) powders have been synthesized by many kinds of methods including hydrothermal condition [4], surfactant-assisted complexation–precipitation approach [11], aqueous salt metathesis reaction [12], precipitation method [13].

There are also a number of applications for functional materials where it is desirable to fabricate the materials in a form of thin films. However little report on the fabrication of $MnWO_4$ thin film with wet chemical methods can be seen in previous literatures. Among the different colloidal processing techniques, electrophoretic deposition (EPD) directly using synthetic nanopowders as deposition resource [14-16] is very promising because it is a fairly rapid, low-cost process for the fabrication of ceramic coatings, monoliths, composites, laminates, and functionally graded materials varying in thickness from a few nanometers to centimeters.

In this work we reported (i) synthesis of $MnWO_4$ nanocrystal using aqueous solution reaction, (ii) the electrophoretic deposition of $MnWO_4$ thin film, and (iii) the luminescent properties of the $MnWO_4$ powders and films.

2. Experimental procedure

For the synthesis of the $MnWO_4$ powder, equimolecular $MnCl_2$ and Na_2WO_4 were respectively dissolved in distilled water, then two solutions was slowly mixed with constant stirring. The brown precipitation was fast formed. After filtering and washing repeatedly with distilled water, the precipitation was then dried at 100 ℃ for 4 h and grinded and partially calcined at temperatures of 400 ℃. Obtained powders were brown and soft.

For the electrophoretic deposition of film, appropriate dried powder were added into a solvent of 2-methoxyethanol and acethylacetone with a volumetric ratio of 9: 1 and then ultrasonicated for 2-4 h with an ultrasonic cleaner (UG, 40kHz, Modal No: KQ-5200DE, China) at 100W to form $MnWO_4$ suspension. The final concentration of the suspension was 0.002 $mol \cdot L^{-1}$. The electrodes used in elecrtophoretic deposition processing were two p-Si(111) substrates of 1.5 cm×1.5 cm with a distance of 1 cm. Before deposition, the substrates were cleaned in ethanol using the ultrasonic cleaner. A dc voltage of 145 V with continuous current of 10 mA was applied to the electrodes in the static suspension for deposition. The as-deposited films were dried at 125 ℃ for 10 min in air.

The phase of the powders was identified at room temperature using X-Ray diffractometer (XRD, $CuK_{\alpha 1}$, λ=0.15406 nm, Model No. D/Max-2200PC, Rigaku, Japan). Scanning electron microscope (SEM, Model No: JXM–6700F, Japan) and transmission electron microscope (TEM, Model No: JEM-3010, Japan) were used to analyze the morphology of the powders and the films. The luminescence properties of the $MnWO_4$ powders and films were measured on the luminescent spectrophotometer (Modal No: LS-55, PE, US).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $MnWO_4$ powders. The hubnerite $MnWO_4$ (PDF: 13-0434) is only XRD detectable phase. The intensity of XRD peaks increased by heating at 400 ℃ for 1h, which corresponds to a little increase in crystallinity of the powders. The calcining at 400 ℃ also resulted in increases of *a*- and *b*-orientation degrees ($I_{(100)}/I_{(-111)}$ from 48.1 to 48.4, $I_{(200)}/I_{(-111)}$ from 12.6 to 16.8, and $I_{(020)}/I_{(-111)}$ from 16.0 to 16.8) and decrease of *c*-orientation degree ($I_{(002)}/I_{(-111)}$ from 58.4 to 55.1). The d-spacing of precipitated and calcined powders determined with XRD analysis were overall larger and smaller respectively than that standard data (PDF: 13-0434) (Table 1). The lattice parameter of the $MnWO_4$ powders calculated with XRD data analyses are respectively a=4.8170, b=5.7420, and c=5.0162 for precipitated powder and a=4.8162, b=5.7276, and c=4.9858 for the calcined powder. It can be seen that the lattice parameter decreased by the calcining at 400 ℃. The average particle size determined with strong (111) peak in XRD pattern decreased from 10.5 nm to 10.1 nm with calcining sample, which can be explained by the corresponding decrease in the lattice parameter. The SEM micrograph of the $MnWO_4$ powders (Fig. 2) indicates that the $MnWO_4$ powders was of small cottony grains. The TEM analysis of the powders (Fig. 3) further revealed that the powders were of rodlike morphology with length of 50 nm and width of 15 nm. Calcining at 400 ℃ changed the rodlike morphology from cuspidal to obtuse and made particle surface smooth.

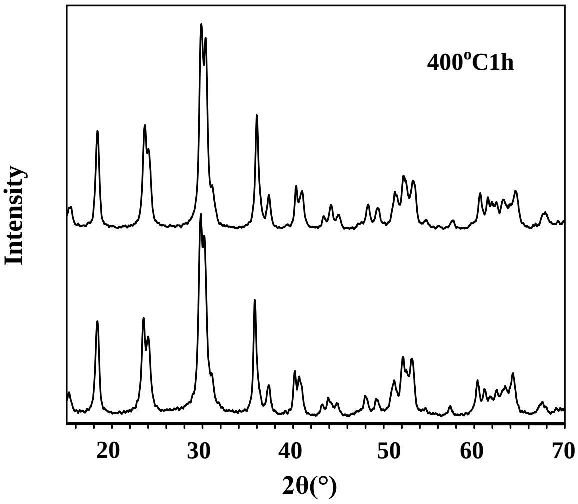
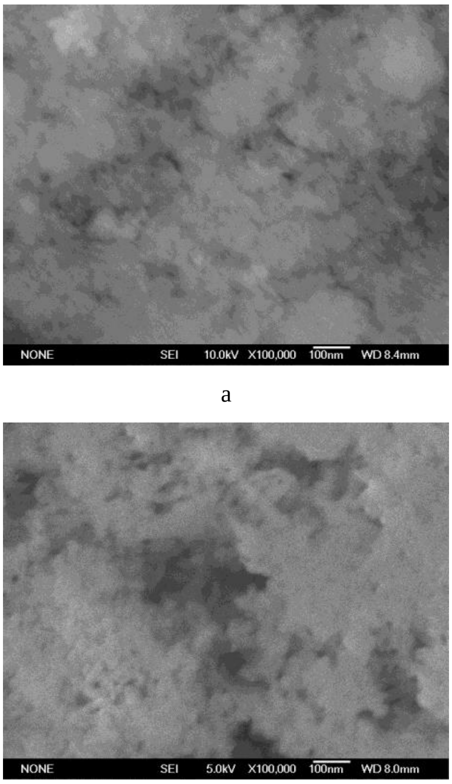


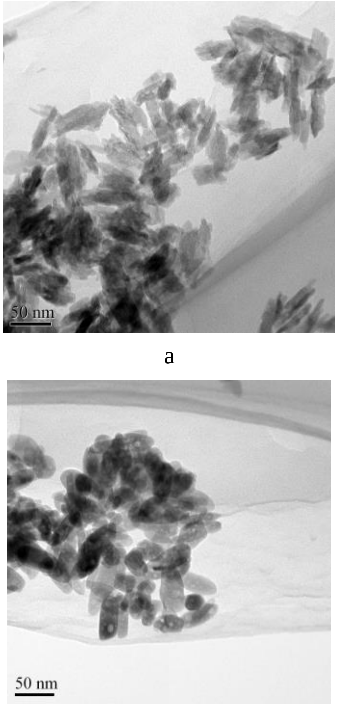
Fig. 1. XRD patterns of the precipitated and 400 ℃-calcined $MnWO_4$ powders.



a

b

Fig. 2. SEM micrographs of the (a) precipitated (b) calcined $MnWO_4$ powders.



a

b

Fig. 3. TEM micrographs of the (a) precipitated (b) calcined $MnWO_4$ powders.

Fig. 4 shows the luminescence properties of the $MnWO_4$ powders measured on the luminescent spectrophotometer. The powders showed a broad excitation band and a broad blue-green emission band. The excitation band was at 208.0 nm (5.96 eV) with a weak band at 238.0 nm (5.21 eV) in the wavelength range used in this measurement. The emission band of $MnWO_4$ powders was centered at 462.7 nm (2.68 eV) and consisted of four strong bands at 425.8 nm (2.91eV), 451.0nm (2.75 eV), 462.7 nm (2.68 eV) and 487.5 nm (2.54 eV), and some weak bands at 514.0 nm (2.41 eV), and 532.0 nm (2.33 eV), etc. Little blue-shift was observed after calcining of 400 ℃, corresponding the decreases in lattice parameter. An obvious increase in intensities of excitation and emission was observed by calcining, which can be attributed the increase in the surface smoothness that can decrease light diffussin.

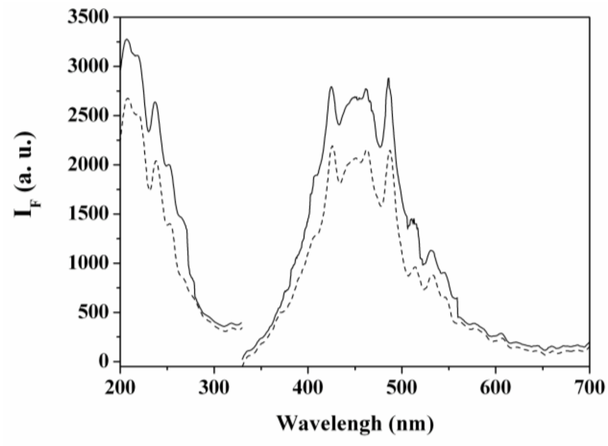


Fig. 4. Excitation-luminescence curves of the precipitated (desh line) and calcined (solid line) $MnWO_4$ powders.

After the $MnWO_4$ suspension was ultrasonicated for 2 h, sediment was observed for 2 h, but when ultrasonicating time was increased to 4 h no sediment was observed in quiescent stage of 12 h. Fig. 5 shows the SEM micrographs of electrophoretic deposited $MnWO_4$ films. The film deposited on the cathode shown homogeneous continues morphology compared to the films deposited on anode. The intensities of excitation and emission of the films were weaker than that of the powders, and appears more intense for the film deposited on the cathode (Fig. 6).

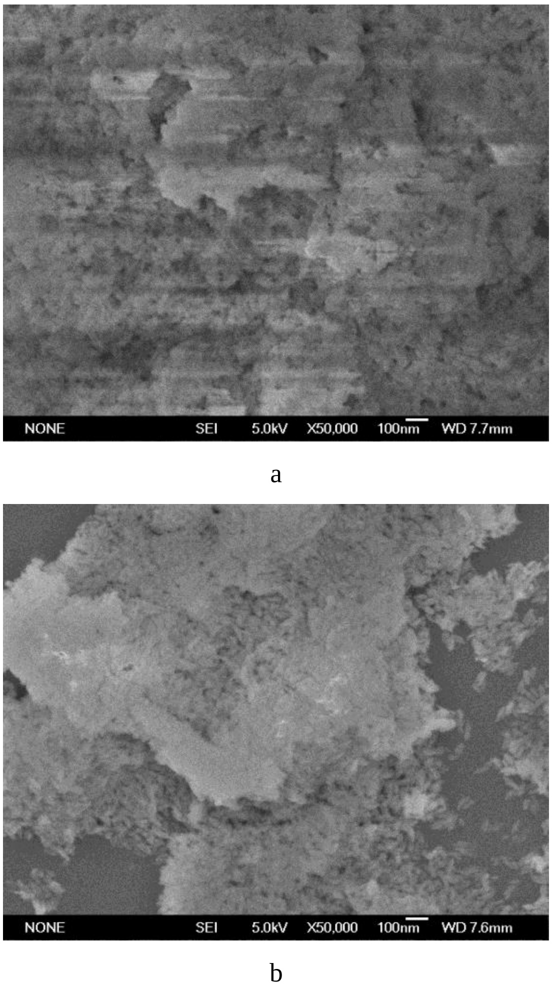


Fig. 5. SEM micrographs of the $MnWO_4$ films electrophoretic deposited on (a) cathode (b) anode.

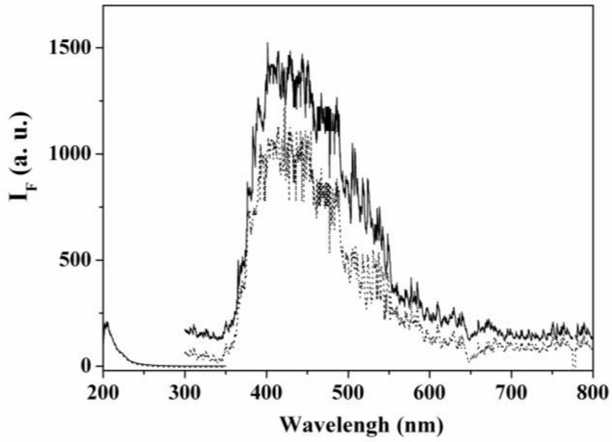


Fig. 6. Excitation-luminescence curves of the $MnWO_4$ films deposited on cathode (solid line) and anode (dot line).

4. Conclusions

Ultrafine $MnWO_4$ powders have been successfully synthesized by aqueous reaction process at room temperature. The powders showed uniform rodlike morphology with particles size about 32 nm and a broad blue-green emission band centered at 462.7 nm (2.68 eV). The calcining at 400 ℃ obviously enhanced the excitation and emission, while the lattice parameter decreases and the surface smoothness increases. Using the precipiated powder as precursor, $MnWO_4$ films were deposited on the p-Si substrate with electrophoretic methods. The films deposited on the cathode appeared more smooth and dense than that on the anode. The intensities in luminescence of the films were about one half of the powder.

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