Research Article

Synthesis of Mo, W, and Mo- and W-Doped Multiwall VONTs via Sol-Gel and Hydrothermal Methods

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Mo, W, and Mo and W were doped into multiwall vanadium oxide nanotubes. The syntheses were performed using sol-gel method followed by hydrothermal method. The synthesized samples were characterized by XRD, SEM, EDX, and TEM techniques. The XRD patterns of the synthesized samples indicated that Mo and W could be doped into VONTs totally up to 50%. The SEM and TEM images showed that the prepared samples have tubular and multiwall morphology and open ends.

1. Introduction

Inorganic nanotubes have potential application in catalytic processes and electrochemical devices [1, 2]. In recent years, inorganic nanotubes have received significant attention [3, 4]. Vanadium oxide nanotubes (VONTs) are one kind of inorganic nanotubes that have application in batteries, sensors, catalysts, and electrochemical devices [5–7]. These nanotubes have been synthesized with various methods such as sol-gel, and hydrothermal [8, 9]. Doping of transition metals into these nanotubes can improve their properties for the desired application for example, “Mo-doped vanadium oxides have found a wide range of applications because of their selective oxidation as well as the unique interaction between V_2O_5 and MoO_3 owing to the similarity of ionic radii and the structures in their highest oxidation state” [9]. Recently, the properties of mixed vanadium-tungsten oxides have been investigated due to their potential use in electrochromic devices [8, 10]. Thus, by doping of both Mo and W into VONTs, new properties for VONTs could be achieved. In this work, Mo doped VONTs up to 20 mol% and W doped VONTs up to 20 mol% and for the first time Mo and W simultaneously were doped into VONTs up to 50 mol%.

2. Material and Method

V_2O_5 (>99%, Merck), MoO_3 (<99%, Merck), H_2WO_4 (<98%, Merck), and $C_{18}H_{39}N$ (~90%, Merck) as a template were used for syntheses of the desired materials. For preparation of $(V_{1-x}M_x)_y$ ONTs ($M = Mo, W, \text{ and } Mo \text{ and } W$) compounds stoichiometric amount of the desired reactants were mixed in distilled water, and the mixture were stirred for 48 h in air. The resulting mixture (gel) was transferred into a teflon-lined autoclave with stainless steel shell. The autoclave was kept at 185°C for 7 days and then allowed to cool naturally. The obtained product was washed with distilled water and absolute ethanol and then dried at 80°C for 8 h. X-ray powder diffraction (XRD) patterns of the prepared samples were obtained using STADI MP X-ray diffractometer with $Cu\ K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). The morphology and quantitative analysis of the samples were studied by scanning electron microscopy (SEM) on Philips XL30 microscope equipped with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) on Philips EM208S microscope operated at 100 kV.

FIGURE 1: XRD patterns of VONTs (a) and Mo-doped VONTs [9] (b).

FIGURE 2: XRD patterns of (a) $V_{0.9}Mo_{0.1}ONTs$ and (b) $V_{0.8}Mo_{0.2}ONTs$ at two different ranges of 2θ ((A) $2\theta = 1-60^\circ$ and (B) $2\theta = 1-10^\circ$).

FIGURE 3: XRD patterns of (a) $V_{0.95}W_{0.05}ONTs$, (b) $V_{0.9}W_{0.1}ONTs$, and (c) $V_{0.8}W_{0.2}ONTs$ at two different ranges of 2θ ((A) $2\theta = 1-60^\circ$ and (B) $2\theta = 1-10^\circ$).

3. Results

The X-ray diffraction (XRD) patterns of $V_{1-x}Mo_xONTs$ ($x = 0.1$ and 0.2), $V_{1-x}W_xONTs$ ($x = 0.05$, 0.1 and 0.2), and $V_{1-(x+y)}Mo_xW_yONTs$ ($x + y = 0.1$, 0.2 , 0.4 and 0.5) are

shown in Figures 2, 3, and 4, respectively. The peaks at $2\theta > 10^\circ$ originate from the two dimensional structure of the walls and nanotubes layers. The XRD patterns of the prepared samples and the comparison of these patterns with that of VONTs [11, 12] (Figure 1) indicate that desired species are

FIGURE 4: XRD patterns of (a) $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs, (b) $V_{0.8}Mo_{0.1}W_{0.1}$ ONTs, (c) $V_{0.6}Mo_{0.2}W_{0.2}$ ONTs, and (d) $V_{0.5}Mo_{0.25}W_{0.25}$ ONTs at two different ranges of 2θ ((A) $2\theta = 1-60^\circ$ and (B) $2\theta = 1-10^\circ$).

FIGURE 5: (a) SEM image, (b) EDX spectrum, and (c) TEM images of $V_{0.95}W_{0.05}$ ONTs.

doped into the vanadium oxide nanotubes. The peak with the highest intensity at the low diffraction angle ($2\theta < 10^\circ$) reflects the inter layer distances of the nanotubes [13]. These patterns indicate that the increase of doping level of the elements into VONTs leads to increasing interlayer distances (Figures 2, 3, and 4) which are considered to be due to the

replacement of V in vanadium oxide nanotubes by Mo and W with larger ionic radii.

Table 1 shows the d_{XRD} values of the most intensive peak for different samples.

The d value of $V_{0.9}W_{0.1}$ ONTs, is relatively similar to that of $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs and the d value of $V_{0.8}W_{0.2}$ ONTs is

FIGURE 6: (a) SEM image, (b) EDX spectrum, and (c) TEM image of $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs.

TABLE 1: The d values of different samples obtained by XRD.

Samples	d_{XRD} (nm)	Samples	d_{XRD} (nm)	Samples	d_{XRD} (nm)
VONTs [9]	3.35	VONTs [9]	3.35	VONTs [9]	3.35
$V_{0.95}W_{0.05}$ ONTs	3.50	$V_{0.9}Mo_{0.1}$ ONTs	4.11	$V_{0.9}Mo_{0.05}W_{0.05}$ ONTs	3.84
$V_{0.9}W_{0.1}$ ONTs	3.86	$V_{0.8}Mo_{0.2}$ ONTs	4.06	$V_{0.8}Mo_{0.1}W_{0.1}$ ONTs	3.91
$V_{0.8}W_{0.2}$ ONTs	3.94			$V_{0.6}Mo_{0.2}W_{0.2}$ ONTs	4.98
				$V_{0.5}Mo_{0.25}W_{0.25}$ ONTs	4.77

TABLE 2: The d values of different samples obtained by XRD and TEM.

Samples	d_{XRD} (nm)	d_{TEM} (nm)
$V_{0.95}W_{0.05}$ ONTs	3.5	2.4
$V_{0.9}Mo_{0.05}W_{0.05}$ ONTs	3.8	2.6

relatively similar to that of $V_{0.9}Mo_{0.1}W_{0.1}$ ONTs. These results indicate that different elements doped into VONTs with the same doping level have nearly the same interlayer distances.

Figures 5(a) and 6(a) show SEM images of $V_{0.95}W_{0.05}$ ONTs and $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs, respectively.

The SEM images indicate that the samples have tubular morphology and nanometric size. The chemical analyses of synthesized samples obtained by EDX are presented in Figures 5(b) and 6(b). The EDX spectra confirm the presence of vanadium, molybdenum, and tungsten in vanadium oxide nanotubes. Figures 5(c) and 6(c) show TEM images of $V_{0.95}W_{0.05}$ ONTs and $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs, respectively. These images indicate that the morphology of both samples is tubular and multiwall. The average measured interlayer distances were 2.4 and 2.6 nm, respectively. The interlayer distances measured using the TEM images, d_{TEM} , and d_{XRD} values of $V_{0.95}W_{0.05}$ ONTs and $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs samples are listed in Table 2. Always d values obtained

from XRD patterns are larger than those of measured from the TEM images [9]. This deviation of d value might be due to a partial rearrangement of the flexible, paraffin-like arrangement of template molecules between the layers under the influence of the electron beam [9].

4. Conclusion

According to our results, doping of Mo, W and Mo and W, into VONTs was successfully prepared by using sol-gel method followed by hydrothermal method, and the synthesized samples had tubular and multiwall morphology with open ends. The results showed that the interlayer distances increased with the increase of doping level of the elements into VONTs. Interlayer distances obtained from the XRD patterns, d_{XRD} are larger than those obtained from the TEM images, d_{TEM} .

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References

- [1] W. Chen, L. Mai, J. Peng, Q. Xu, and Q. Zhu, "Raman spectroscopic study of vanadium oxide nanotubes," *Journal of Solid State Chemistry*, vol. 177, no. 1, pp. 377–379, 2004.
- [2] W. Chen, L. Mai, Y. Qi, and Y. Dai, "One-dimensional nanomaterials of vanadium and molybdenum oxides," *Journal of Physics and Chemistry of Solids*, vol. 67, no. 5-6, pp. 896–902, 2006.
- [3] C. J. Cui, G. M. Wu, H. Y. Yang et al., "A new high-performance cathode material for rechargeable lithium-ion batteries: polypyrrole/vanadium oxide nanotubes," *Electrochimica Acta*, vol. 55, no. 28, pp. 8870–8875, 2010.
- [4] C. J. Cui, G. M. Wu, J. Shen et al., "Synthesis and electrochemical performance of lithium vanadium oxide nanotubes as cathodes for rechargeable lithium-ion batteries. , -," *Electrochimica Acta*, vol. 55, pp. 2536–2541, 2010.
- [5] J. Emmerich, M. Dillen, C. E. A. Kirschhock, and J. A. Martens, "Fine-tuning of vanadium oxide nanotubes," *Studies in Surface Science and Catalysis*, vol. 175, pp. 249–252, 2010.
- [6] A. V. Grigorieva, A. B. Tarasov, E. A. Goodilin et al., "Sensor properties of vanadium oxide nanotubes," *Mendeleev Communications*, vol. 18, no. 1, pp. 6–7, 2008.
- [7] M. Roppolo, C. B. Jacobs, S. Upreti, N. A. Chernova, and M. S. Whittingham, "Synthesis and characterization of layered and scrolled amine-templated vanadium oxides," *Journal of Materials Science*, vol. 43, no. 14, pp. 4742–4748, 2008.
- [8] F. Li, X. Wang, C. Shao, R. Tan, and Y. Liu, "W doped vanadium oxide nanotubes: synthesis and characterization," *Materials Letters*, vol. 61, no. 6, pp. 1328–1332, 2007.
- [9] L. Q. Mai, W. Chen, Q. Xu, J. F. Peng, and Q. Y. Zhu, "Mo doped vanadium oxide nanotubes: microstructure and electrochemistry," *Chemical Physics Letters*, vol. 382, no. 3-4, pp. 307–312, 2003.
- [10] L. F. Jiao, H. T. Yuan, Y. C. Si, Y. J. Wang, and Y. M. Wang, "Synthesis of Cu_{0.1}-doped vanadium oxide nanotubes and their application as cathode materials for rechargeable magnesium batteries," *Electrochemistry Communications*, vol. 8, no. 6, pp. 1041–1044, 2006.
- [11] W. Chen, J. Peng, L. Mai, Q. Zhu, and Q. Xu, "Synthesis of vanadium oxide nanotubes from V₂O₅ sols," *Materials Letters*, vol. 58, no. 17-18, pp. 2275–2278, 2004.
- [12] L. Mai, W. Chen, Q. Xu, Q. Zhu, C. Han, and J. Peng, "Cost-saving synthesis of vanadium oxide nanotubes," *Solid State Communications*, vol. 126, no. 10, pp. 541–543, 2003.
- [13] F. Sediri, F. Touati, and N. Gharbi, "A one-step hydrothermal way for the synthesis of vanadium oxide nanotubes containing the phenylpropylamine as template obtained via non-alkoxide route," *Materials Letters*, vol. 61, no. 8-9, pp. 1946–1950, 2007.