Research Article

Synthesis of Mo, W, and Mo- and W-Doped Multiwall VON Ts 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 VON Ts 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 (VON Ts) 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 V2O5 and MoO3 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 VON Ts, new properties for VON Ts could be achieved. In this work, Mo doped VON Ts up to 20 mol% and W doped VON Ts up to 20 mol% and for the first time Mo and W simultaneously were doped into VON Ts up to 50 mol%.

2. Material and Method

V2O5 (>99%, Merck), MoO3 (<99%, Merck), H2WO4 (<98%, Merck), and C18H35N (∼90%, Merck) as a template were used for syntheses of the desired materials. For preparation of (V1−xMx)yONTs (M = Mo, W, and Mo 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 Kα radiation (λ = 1.5406 Å). 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.
3. Results

The X-ray diffraction (XRD) patterns of $V_{1-x}Mo_x$ ONTs ($x = 0.1$ and 0.2), $V_{1-x}W_x$ ONTs ($x = 0.05$, 0.1 and 0.2), and $V_{1-(x+y)}Mo_xW_y$ ONTs ($x + y = 0.1$, 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 three-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
doped into the vanadium oxide nanotubes. The peak with the highest intensity at the low diffraction angle \((2\theta < 10^\circ)\) reflects the interlayer 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 \(d_{\text{XRD}}\) 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

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Figure 4: XRD patterns of (a)\(V_{0.9}Mo_{0.05}W_{0.05}\) ONTs, (b) \(V_{0.9}Mo_{0.1}W_{0.1}\) 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 \(2\theta\) ((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.
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 $V_{0.9}W_{0.05}$ 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, $d_{\text{TEM}}$, and $d_{\text{XRD}}$ values of $V_{0.9}W_{0.05}$ ONTs and $V_{0.9}Mo_{0.05}W_{0.05}$ ONTs samples are listed in Table 2. Always $d$ values obtained 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.

**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.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_{\text{XRD}}$ (nm)</th>
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<th>$d_{\text{XRD}}$ (nm)</th>
<th>Samples</th>
<th>$d_{\text{XRD}}$ (nm)</th>
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<tbody>
<tr>
<td>$V_{0.95}W_{0.05}$ ONTs</td>
<td>3.50</td>
<td>$V_{0.9}Mo_{0.1}$ ONTs</td>
<td>4.11</td>
<td>$V_{0.9}Mo_{0.05}W_{0.05}$ ONTs</td>
<td>3.84</td>
</tr>
<tr>
<td>$V_{0.9}$ ONTs</td>
<td>3.66</td>
<td>$V_{0.8}$ Mo ONTs</td>
<td>4.06</td>
<td>$V_{0.8}Mo_{0.1}$ ONTs</td>
<td>3.91</td>
</tr>
<tr>
<td>$V_{0.8}$ W ONTs</td>
<td>3.94</td>
<td>$V_{0.6}$ Mo ONTs</td>
<td>4.98</td>
<td>$V_{0.6}Mo_{0.2}$ ONTs</td>
<td>4.77</td>
</tr>
</tbody>
</table>

**Table 2:** The $d$ values of different samples obtained by XRD and TEM.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_{\text{XRD}}$ (nm)</th>
<th>$d_{\text{TEM}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{0.95}W_{0.05}$ ONTs</td>
<td>3.5</td>
<td>2.4</td>
</tr>
<tr>
<td>$V_{0.9}Mo_{0.05}W_{0.05}$ ONTs</td>
<td>3.8</td>
<td>2.6</td>
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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, $d_{\text{XRD}}$, are larger than those obtained from the TEM images, $d_{\text{TEM}}$.

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References


