Synthesis of Mo, W and Mo and W doped multiwall VONTs via sol-gel and hydrothermal methods

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Abstract

Introduction: Vanadium oxide nanotubes (VONTs) have many applications in batteries, catalysts and electrochemical devices. Doping of transition metals into these nanotubes can improve their properties for the desired application.

Aim: Synthesis and characterization of molybdenum and tungsten doped vanadium oxide nanotubes

Material and Method: V_2O_5, MoO_3, H_2WO_4 and $C_{18}H_{39}N$ were used for synthesizing the desired materials. For preparation of $(V_{1-x}M_x)_yONTs$ (M= Mo, W and Mo&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 slurry was transferred into an autoclave and was kept at 185 °C for 7 days. The obtained product was washed and dried at 80 ºC for 8 h.

Results: The XRD patterns of the prepared samples and the comparison of these patterns with that of VONTs indicate that desired species were doped into the vanadium oxide nanotubes. The SEM images indicated that, the samples had tubular morphology and nanometric size. The presence of vanadium, molybdenum and tungsten in vanadium oxide nanotubes were confirmed by the EDX spectra.TEM images indicated that the morphology of samples is tubular and multiwall.

Conclusion: In this research, Mo, W and Mo & W, were doped into multiwall vanadium oxide nanotubes. the synthesized samples had tubular and multiwall morphology with open ends.

***Keywords*:** multiwall vanadium oxide nanotubes, molybdenum and tungsten

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]

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These nanotubes have been synthesized with various methods, such as sol – gel, hydrothermal, etc..[8-9] Doping of transition metals into these nanotubes can improve their properties for the desired application e.g. "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%.

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 synthesis of the desired materials. For preparation of $(V_{1-x}M_x)_y$ONTs (M = Mo, W and Mo&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 ºC 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.

Results and discution

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 = 0.05, 0.1, 0.2 and 0.25) are shown in Figs. 2, 3 and 4, respectively. The peaks at 2θ>10º 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, 13] (Fig. 1) indicate that desired species are doped into the vanadium oxide nanotubes. The peak with the highest intensity at the low diffraction angle (2θ<10º) reflects the inter layer distances of the nanotubes [12]. These patterns indicate that the increase of doping level of the elements into VONTs leads to increasing interlayer distances (Figs. 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.

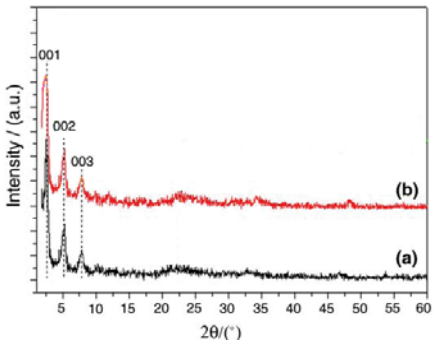
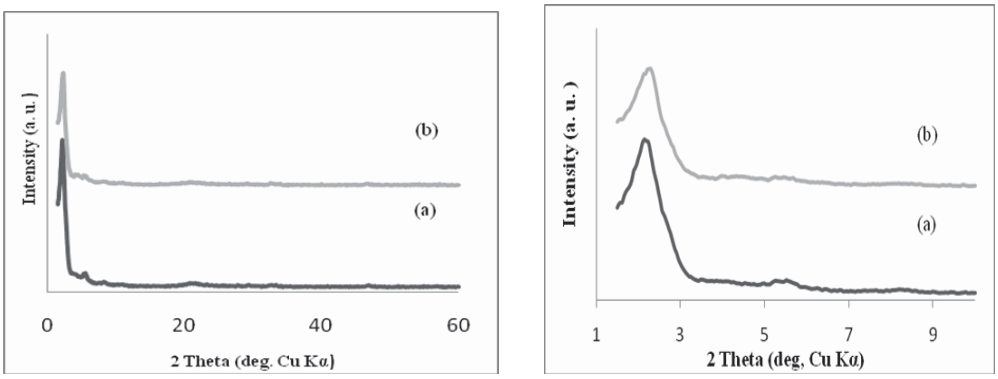
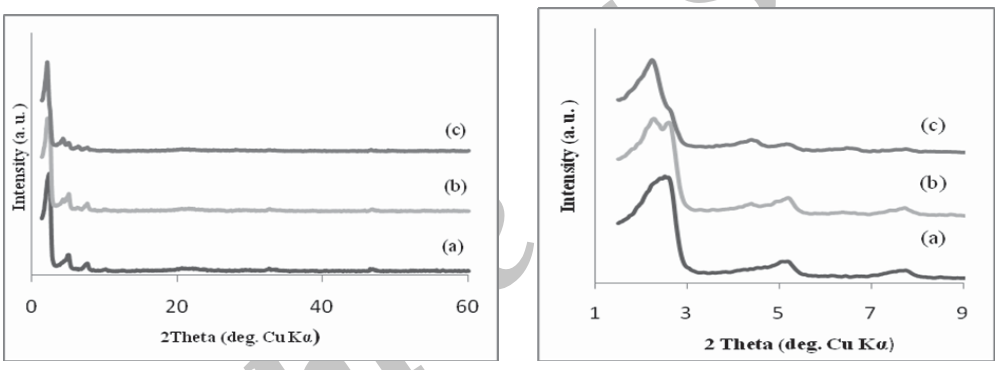


Fig. 1- XRD patterns of VONTs (a) and Mo doped VONTs [9] (b)



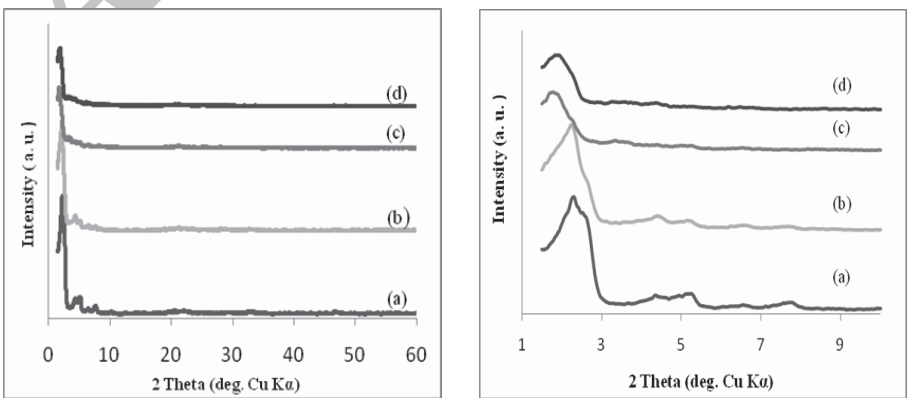
(A) (B)

Fig. 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 2 ((A) 2 =1-60° and (B) 2 =1-10°)



(A) (B)

Fig. 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 2 ((A) 2 =1-60° and (B) 2 =1-10°)



(A) (B)

Fig. 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 2 ((A) 2 =1-60° and (B) 2 =1-10°)

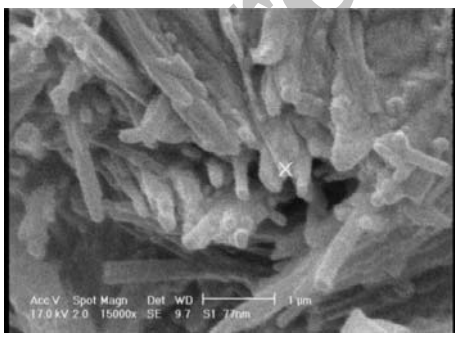
Table 1 shows the d_{XRD} values of the most intensive peak for different samples.

Table 1- The *d* values of different samples obtained by XRD

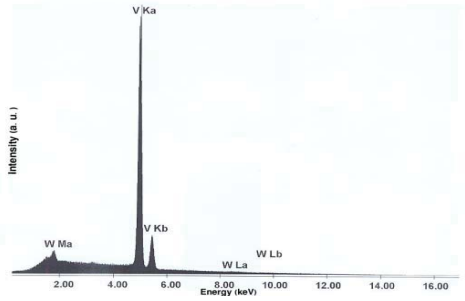
Samples	d_{XRD} **(nm)**	**Samples**	d_{XRD} **(nm)**	**Samples**	d_{XRD} **(nm)**
VONTs [9]	3.35	VONTs [9]	3.35	VONTs [9]	3.35
$V_{0.95}W_{0.05}$ONTs	3.50	$V_{0.9}Mo_{0.1}$ONTs	4.11	$V_{0.9}Mo_{0.05}W_{0.05}$ONTs	3.84
$V_{0.9}W_{0.1}$ONTs	3.86	$V_{0.8}Mo_{0.2}$ONTs	4.06	$V_{0.8}Mo_{0.1}W_{0.1}$ONTs	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

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 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.

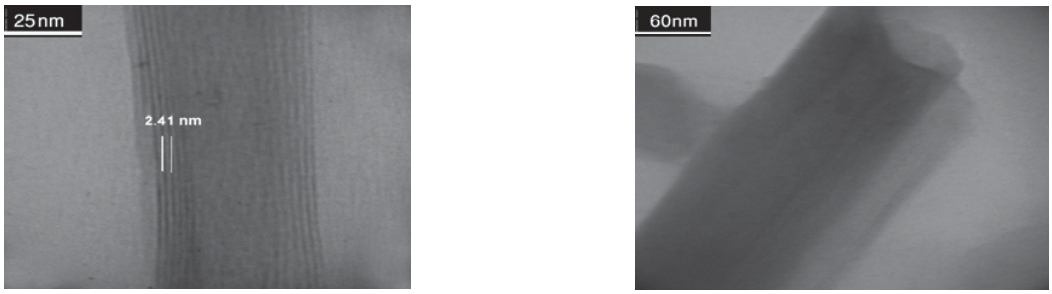
Figs. 5A and 6A show SEM images of $V_{0.95}W_{0.05}$ONTs and $V_{0.9}Mo_{0.05}W_{0.05}$ONTs, respectively. The SEM images indicate that, the samples have tubular morphology and nanometric size. The chemical analyses of synthesized samples obtained by EDX are presented in Figs. 5B and 6B. The EDX spectra confirm the presence of vanadium, molybdenum and tungsten in vanadium oxide nanotubes. Figs. 5C and 6C 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]



A

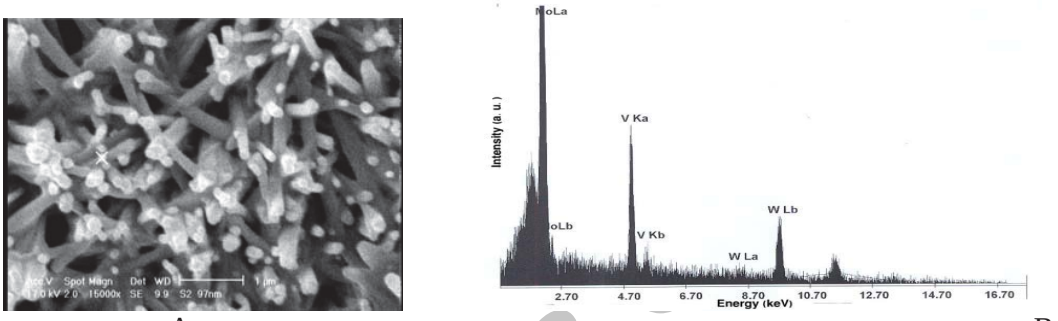


B

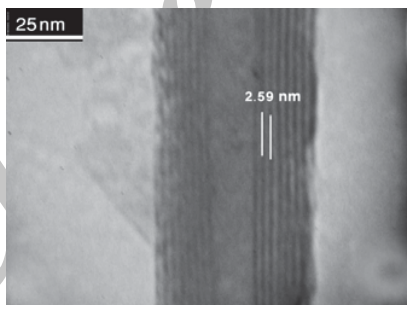


C

Fig. 5 - (A) SEM image, (B) EDX spectrum and (C) TEM images of $V_{0.95}W_{0.05}$ONTs



A B



C

Fig. 6 - (A) SEM image, (B) EDX spectrum and (C) TEM image of $V_{0.9}Mo_{0.05}W_{0.05}$ONTs

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

Conclusion

According to our results, doping of Mo, W and Mo & W into VONTs were 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 of obtained from the TEM images, d_{TEM}.

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