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Raman spectroscopic study of vanadium oxide nanotubes

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Abstract

Raman-scattering measurements have been used to study the microstructure of vanadium oxide nanotubes (VO_x-NTs). The Raman spectra of VO_x-NTs reflect the various (group) vibrations of V–O type and lattice vibration of the layered structure as well as organic group vibration of the residual organic template. Moreover, it is confirmed that the residual organic template can be removed by irradiation of laser under the preservation of the tubular morphology, which provides the possibility for favoring the scaling-up of removing the residual organic template in the structure of VO_x-NTs.

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Keywords: Raman; Microstructure; Vanadium oxides; Residual organic template; Laser irradiation

1. Introduction

Since Iijima discovered carbon nanotubes in 1991 [1], considerable attention has been drawn towards one-dimensional (1D) nanostructure materials, such as nanotubes, nanowires and nanorods, because of both their interesting physicochemical properties and the wide range of their potential applications in the nanodevices [2,3]. The recently discovered vanadium oxide nanotubes (VO_x-NTs) are especially interesting since vanadium oxides are widely applied in electrochemical devices and catalysis [4]. Recently, we synthesized the VO_x-NTs in a rheological phase reaction followed by self-assembling process, but it was found that there were residual organic templates in as-synthesized VO_x-NTs, which would be harmful to their properties [5,6]. Laser Raman spectroscopic study has successfully been employed to study the microstructures of transition metal oxide thin films [7,8]. In this paper, Raman-scattering measurements have been used to examine the microstructure of VO_x-NTs. Meanwhile, the interesting result is reported that the residual organic template in the structure of VO_x-NTs can be removed by proper laser irradiation under the preservation of tubular morphology of VO_x-NTs.

2. Experimental

VO_x-NTs were prepared via a rheological phase reaction followed by self-assembling process as previously described [5]. V₂O₅ of 10 mmol and 10 mmol hexadecylamine was mixed with 5 mL distilled water. After stirring for 1 h, 15 mL distilled water was added to the orange solution. After aging for 48 h, the resulting rheological suspension was transferred into a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 180°C for about a week. The final black product was washed with distilled water and dried at 80°C for 8 h.

XRD experiments were done on a D/MAX-III X-ray diffractometer with CuK α radiation and graphite monochromator. TEM image was taken in a JEOL JEM-2010FEF microscope operated at 200 kV. The Raman spectra were taken on a Renishaw RM-1000 laser Raman microscope system. Excitation was with a 40 mW 514.5 nm Ar-ion laser (amount of power on sample is about 5 mW). Both the spectral resolution and the accuracy in the Raman shift are estimated to be $\sim 2 \text{ cm}^{-1}$.

3. Results and discussion

The Raman spectra of the as-synthesized and laser-irradiating samples are shown in Fig. 1. For the former,

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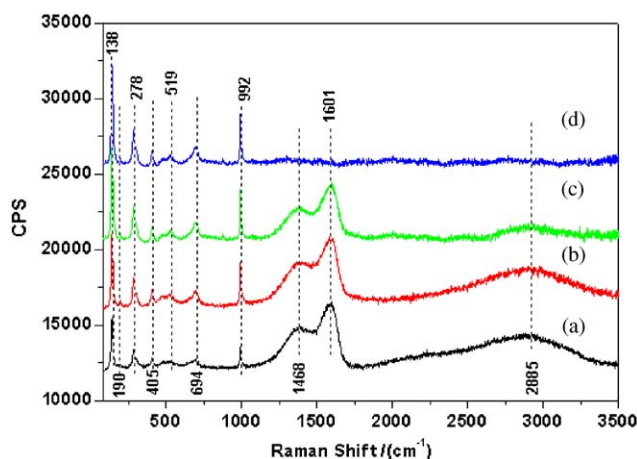


Fig. 1. Raman spectra of the as-synthesized sample (a) and its laser-irradiating products at 5 min (b), 8 min (c) and 15 min (d).

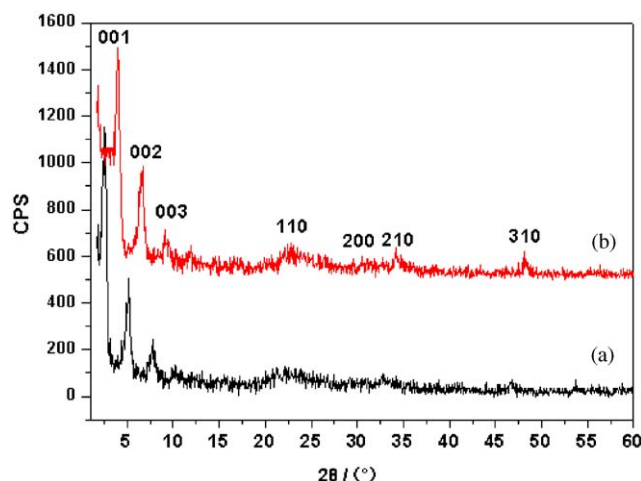


Fig. 2. XRD patterns of the as-synthesized sample (a) and its laser-irradiating product at 15 min (b).

the Raman spectrum in the range of 100–3000 cm^{-1} is dominated by the peaks at 138, 992, 1468, 1601, 2885 cm^{-1} , respectively. The peak at 992 cm^{-1} corresponds to the terminal oxygen ($\text{V}=\text{O}$) stretching mode which results from an unshared oxygen [9]. The peak at 694 cm^{-1} is assigned to the doubly coordinated oxygen ($\text{V}_2\text{-O}$) stretching mode which results from corner-shared oxygens in common to two pyramids [10]. The peak at 519 cm^{-1} is assigned to the triply coordinated oxygen ($\text{V}_3\text{-O}$) stretching mode which results from edge-shared oxygens in common to three pyramids [10,11]. The two peaks located at 405 and 278 cm^{-1} are assigned to the bending vibration of the $\text{V}=\text{O}$ bonds [10]. The peak located at 484 and 303 cm^{-1} are assigned to the bending vibration of the bridging V-O-V (doubly coordinated oxygen), and the triply coordinated oxygen ($\text{V}_3\text{-O}$) bonds, respectively [10]. Two more low-frequency Raman peaks at 194 and 138 cm^{-1} is assigned to the stretching mode of $(\text{V}_2\text{O}_2)_n$ which correspond to the chain translation [10]. The two peaks are strongly associated with the layered structure [11,12], which is in agreement with the result of XRD (see Fig. 2). The peaks at 2885, 1601 and 1468 cm^{-1} can be unambiguously assigned to the presence of residual organic template in the structure [13,14]. The intensity of these peaks decreases with the laser-irradiating time and disappears completely at 15 min, which suggests that the residual organic template has been removed while the structure of vanadium oxide in the as-synthesized sample is not destroyed because there are no noticeable change for the peaks between 100 and 1000 cm^{-1} corresponding to the various (group) vibrations of V-O type.

In order to further support the above conclusion, the XRD measurements were performed. The XRD patterns of the as-synthesized sample and its 15-min laser-irradiating product are shown in Fig. 2. It can be seen that there are no significant differences between them

and two set of diffraction patterns are observed in both of them: the $00l$ one corresponding to a well-ordered layer structure and $hk0$ one corresponding to the two-dimensional structure of the VO_x layers which form the walls of the VO-NTs . However, in contrast with the as-synthesized sample, there is a noticeable shift of the $00l$ peak toward higher diffraction angle for its 15-min laser-irradiating product. It is suggested that the distance between the vanadium oxide layers decreases from 3.35 to 2.10 nm, owing to the removal of residual organic template from the laser irradiation. TEM investigation confirms that the tubular morphology is preserved, as shown in Fig. 3.

4. Conclusions

In summary, the Raman spectra of $\text{VO}_x\text{-NTs}$ show two peaks around 519 and 694 cm^{-1} , due to the stretching modes of the $\text{V}_3\text{-O}$ and $\text{V}_2\text{-O}$ bonds, respectively, and a relatively sharp peak at 992 cm^{-1} due to the $\text{V}=\text{O}$ stretching mode of terminal oxygen atoms. Two low-frequency peaks at 194 and 138 cm^{-1} are strongly associated with the layered structure. Moreover, the Raman peaks at 2885, 1601 and 1468 cm^{-1} can be assigned to the presence of residual organic template in the structure. Raman spectroscopic study for the laser-irradiating product at different time as well as XRD and HRTEM investigations confirms that the residual organic template can be removed under the preservation of nanotube structure, which open a new method for favoring the scaling-up of removing the residual organic template in the structure of $\text{VO}_x\text{-NTs}$ and functionalizing the highly anisotropic tubular structure because of the simplicity and availability of laser irradiation.

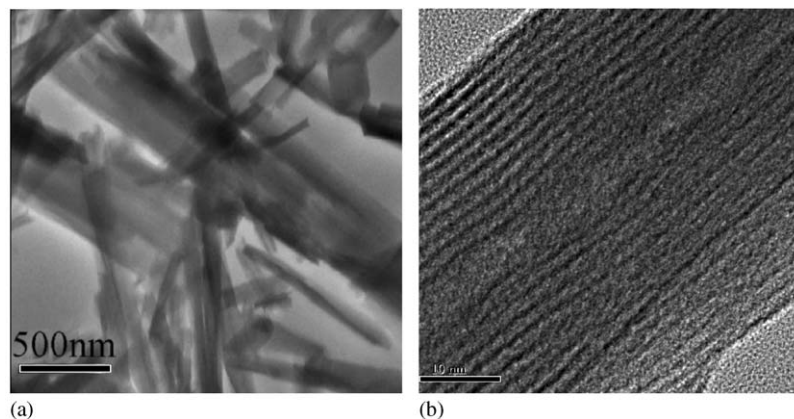


Fig. 3. TEM image of the laser-irradiating product at 15 min: (a) general view, (b) high-magnification image showing both a tubular morphology and its multiwalled structure.

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