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ScienceDirect
Electrochemistry Communications 9 (2007) 1766–1771
electrochemistry communications
www.elsevier.com/locate/elecom

# Vanadium-oxide nanotubes: Synthesis and template-related electrochemical properties

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Received 15 March 2007; received in revised form 30 March 2007; accepted 31 March 2007
Available online 12 April 2007

**Abstract**

The electrochemistry of mixed-valent-containing vanadium-oxide nanotubes ($VO_x$-NTs) is first reported. Using dodecylamine and hexadecylamine as templates, two kinds of $VO_x$-NTs were synthesized and characterized. Both $VO_x$-NTs contain $V_2O_3$, $VO_2$ and $V_2O_5$ species. Dodecylamine-templated $VO_x$-NTs ($C_{12}$-$VO_x$-NTs) are much more stable than hexadecylamine-templated $VO_x$-NTs ($C_{16}$-$VO_x$-NTs). $C_{12}$-$VO_x$-NTs demonstrate stable redox behavior at $\sim -0.2$ V, which is arising from the electrochemical transfer between V(III) and V(IV), whereas $C_{16}$-$VO_x$-NTs exhibit unstable and weak redox peaks. In both cases, the reduction reaction of V(V)–V(IV) is never observed. The oxidation peak for V(IV) appeared only after a relatively long time immersion, suggesting that some small molecules such as water intercalate into the layered nanostructures before the electrochemical reaction. The difference may be an origin of the different template-induced the electroactivity of vanadium-oxide species in the nanotube-microenvironment.


*Keywords:* Vanadium-oxide nanotubes; Template; Mixed-valents; Electrochemical properties

## 1. Introduction

Over the past decade, nanostructured materials have become a symbol of the new and fast developing research area of nanotechnology [1,2]. These novel nanosturctured materials aroused intense interest due to their extraordinary physical and chemical properties that may be developed for a variety of real applications. Among them, the tubular morphology is particularly attractive since it provides access to the three different contact regions: inner and outer surface as well as the tube ends [3]. Therefore, it holds great advantage over nanoparticles in exploring nano-devices. Very recently, the preparation of transition-metal-oxide nanotubes (NTs) such as titanium-dioxide NTs ($TiO_2$-NTs and titanate NTs) [4,5] and vanadium-oxide NTs ($VO_x$-NTs) has been carried out; however, their applications are still under the way. The importance of the development of these transition-metal NTs lies in their displaying a number of oxidation states with possible redox-active properties. Actually, the electrochromism and electrochemical properties as well as their applications in electrochemical sensors of $TiO_2$-NTs and titanate NTs had been developed [6]. We recently found that the nanochannels of titanate mesoporous composite may provide environment for the intercalation of proton in the transferring of Ti(IV) to Ti(III) with electrons accumulation [7]. Vanadium displays a number of oxidation states and can thus form a wide variety of single-, and mixed-valent compounds with different properties [8,9]. It was reported that the sheet distance between the layers of the scroll affected

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doi:10.1016/j.elecom.2007.03.027

the optical properties of vanadate-nanotube [10]. However, the electrochemical properties $VO_x$-NTs have seldom been reported. Therefore, it is of great significance to study $VO_x$-based nanotubes by exploiting their possible applications in catalytic and electrochemical aspects. In the present study, $VO_x$-based nanotubes were prepared by using dodecylamine and hexadecylamine as templates. The electrochemical properties of two kinds of $VO_x$-NTs were compared. Our finding suggests that the longer template leads instability of the NTs.

## 2. Experimental

### 2.1. Materials

Vanadium (V) pentoxide, dodecylamine and hexadecylamine were obtained from Wako Chemical Co. (Tokyo, Japan) and used without further purification. Chitosan and *N*,*N*-dimethylacetamide (DMAA) were purchased from Wako Chemical Co. and used as received. Nafion solution (5%, w/w) was obtained from ElectroChem. Inc. (Woburn, MA, USA). *N*-2-Hydroxyethylpiperazine–*N*′-2-ethanesulfonic acid (HEPES) was obtained from Dojido Laboratories (Kumamoto, Japan).

### 2.2. Synthesis of $VO_x$-NTs from vanadium pentoxide

$VO_x$-NTs were prepared on basis of a published procedure [8] with modification. Briefly, a suspension of $V_2O_5$ (10 mmol) and a primary amine $C_nH_{2n+1}NH_2$ ($n = 12$ or 16; molar ratio 1:1, i.e., V:template = 2:1) in 5 mL of 7:3 (v/v) ethanol–water was stirred for 2 h. Water (15 ml) was added to this mixture and continued to stir for 48 h. The resulting composite was transferred into Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 180 °C for 7 days. The generated black product was successively washed with ethanol and hexane; finally dried at 70 °C at ambient condition.

### 2.3. Characterization

Both transmission electron microscope (TEM) and scanning electron microscope (SEM) measurements were conducted using a JEM-2000EXII (JEOL Co. Ltd.) and Leo Gemini Supra 35 scanning electron microscopy (Carl Zeiss), respectively. X-ray powder diffraction (XRD) pattern was done with a Mo3XHF22 (MAC Science Co. Ltd., UK). X-ray Photoelectron Spectroscopy (XPS) was used to determine the possible vanadium states in the synthesized nanotubes.

### 2.4. Preparation of $VO_x$-NTs composite suspension

In a typical procedure, 4-mg $VO_x$-NTs was added into a mixture of 0.2-mL ethanol and 1-mL chitosan solution (pH 6, 2 mg/ml), then mixed well under sonication for at least 30 min. After that, a composite suspension is obtained.

### 2.5. Fabrication of $VO_x$-NT composite film-covered PG electrode

Prior to coating, the basal plane pyrolytic graphite (PG) disk electrodes (3-mm diameter) were polished with 800-grit sandpaper, washed, and further sonicated in Milli-Q water. A 15-μL aliquot of the thus-prepared composite was uniformly cast onto the inverted PG disk electrode. In order to discuss the effect of loading amount of nanotubes, the electrode surface was coated with a 30-μL aliquot of the composites. The thus-modified electrodes were air-dry overnight before use.

### 2.6. Electrochemical measurements

The electrochemical response was measured in a conventional three-electrode system using a modified PG electrode as working electrode, a platinum wire as counter electrode, and a Ag/AgCl (3.3 M KCl) electrode as reference electrode. All potentials were reported in this context with respect to this reference. For cyclic voltammetric (CV) measurements, an Autolab potentiostat/galvanostat (Eco Chemie, B. V, Utrecht, The Netherlands) was used. All measurements were performed at room temperature (~20 °C).

## 3. Results and discussion

### 3.1. Synthesis and characterization of vanadium-oxide nanotubes

Vanadium-oxide nanotubes ($VO_x$-NTs) were prepared by using primary monoamines ($C_nH_{2n+1}NH_2$, $6 \leqq n \leqq 20$) as structure-directing templates [3,8,11]. In the present research, dodecylamine-templated $VO_x$-NTs ($C_{12}$-$VO_x$-NTs) and hexadecylamine-templated $VO_x$-NTs ($C_{16}$-$VO_x$-NTs) were obtained using vanadium(V) pentoxide and precursors of dodecylamine as well as hexadecylamine in a modified condition. The yield of the template-supporting $VO_x$-NTs was calculated to be ~80%. The scanning electron microscope (SEM) images for the as-prepared $C_{12}$-$VO_x$-NTs and $C_{16}$-$VO_x$-NTs are shown in Fig. 1. The nanotubes are grown together in bundles with typical nanotube lengths ranging from 1 to 8 μm. Fig. 2 shows the transmission electron microscope (TEM) images for the as-prepared $C_{12}$-$VO_x$-NTs and $C_{16}$-$VO_x$-NTs. A single nanotube is composed of 5–30 layered walls. The prepared nanotubes are generally two-end-open with inner diameter of 15–30 nm and outer diameter of 60–100 nm. The X-ray powder diffraction (XRD) patterns for the $C_{12}$-$VO_x$-NTs and $C_{16}$-$VO_x$-NTs are very similar; the low-angle reflection peaks are characteristic of the well-ordered layered structures (Fig. 3). These observations show that there is no obvious morphological difference between $C_{12}$-$VO_x$-NTs and $C_{16}$-$VO_x$-NTs, though the templates are different. The distances between vanadium-oxide layers are calculated from the *d* values of the *001* reflection peak in XRD patterns. The interlayer distances are 2.72 and