Reviews

Synthesis and Enhanced Intercalation Properties of Nanostructured Vanadium Oxides

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Nanomaterials lie at the heart of the fundamental advances in efficient energy storage/conversion and other types of nanodevices in which the surface process and transport kinetics play determining roles. This review describes some recent developments in the synthesis and characterizations of various vanadium oxide nanostructures including nanowires, nanorolls, nanobelts, and ordered arrays of nanorods, nanotubes, and nanocables for significantly enhanced intercalation properties. The major topic of this article is to highlight the lithium ion intercalation properties of nanostructured vanadium oxides for energy storage as well as other applications in sensors, actuators, and transistors.

1. Introduction

The technological limits of present microdevices have stimulated wide research activities targeted at downsizing the devices by at least an order of magnitude, and nanomaterials are the perfect building blocks for this purpose. The reduction in the necessary amount of functional materials leads to reduction of toxicity and less use of resources. Most importantly, nanomaterials offer the unusual mechanical, electrical, and optical properties endowed by confining the dimensions of such materials, and the overall behavior of nanomaterials exhibits combinations of bulk and surface properties.1 Thus, nanostructured materials are drawing a tremendous amount of attention because of their novel properties and because of their potential applications in various nanodevices, such as field-effect transistors (FETs)2–5 chemical and biological sensors,6–9 nanopores,10 and nanocables.11 Furthermore, the emerging energy resource crisis and ecological concerns unambiguously show that energy storage is one of the great challenges in the current century. It is critical that low-cost, lightweight, small-volume, and environment friendly energy storage/conversion devices are developed, and nanomaterials are attracting great interest for electrochemical energy storage, for example, the rechargeable lithium ion batteries. The reports on the processing, properties, and applications of nanomaterials are rapidly appearing on a daily basis. The purpose of the present work is to give an in-depth survey of recent progress on synthesis and characterizations of nanomaterials by choosing vanadium pentoxide (V₂O₅) as a model material system. As a result of the multiple valence state of vanadium oxide, vanadium pentoxide has versatile redox-dependent properties and finds wide applications in catalysis,12 electrochromism,13–15 and electrochemistry.16–18 The nanostructured form of this material has been employed in FETs,19 sensors,20,21 spintronic devices,22 and nanolithography templates.23,24

Vanadium pentoxide is a typical intercalation compound as a result of its layered structure. Intercalation compounds are a special family of materials. The intercalation refers to the reversible intercalation of mobile guest species (atoms, molecules, or ions) into a crystalline host lattice that contains an interconnected system of an empty lattice site of appropriate size, while the structural integrity of the host lattice is formally conserved.25 The intercalation reactions typically occur around room temperature. A variety of host lattice structures have been found to undergo such low-temperature reactions.26 However, the intercalation reactions involving layered host lattices have been most extensively studied, partly because of the structural flexibility and the ability to adapt to the geometry of the intercalated guest species by free adjustment of the interlayer separation. The readers are referred to a comprehensive and excellent article on inorganic intercalation compounds.25 Despite the differences in chemical composition and lattice structure of the host sheets, all the layer hosts are characterized by strong interlayer covalent bonding and weak interlayer intercalations. The weak interlayer intercalations include van der Waals force or electrostatic attraction through oppositely charged species between two layers. Various host lattices are metal dichalcogenides, metal oxyhalides, metal phosphorus trisulfides, metal oxides, metal phosphates, hydrogen phosphates, phosphonates, and graphite and layered clay minerals. Guest materials include metal ions, organic molecules, and organometallic molecules. When guest species are incorporated into host lattices, various structural changes will take place. The principle geometrical transitions of layered host lattice matrixes upon intercalation
of guest species include (1) change in interlayer spacing, (2) change in stacking mode of the layers, and (3) formation of intermediate phases at low guest concentrations that may exhibit staging.27 There are various synthesis methods for the formation of intercalation compounds,25,28 The most commonly used and simplest method is the direct reaction.29 For direction reactions, the intercalation reagents must be good reducing agents of the host crystals.30 Appropriate chosen solvents or electrolytes may assist the ion exchange reactions by flocculating and reflocculating the host structure.31 Electrointercalation is yet another method, in which the host lattice serves as the cathode of an electrochemical cell.32 Electrochemical lithium intercalation occurs together with compensating electrons leading to the formation of vanadium bronzes as follows:

$$V_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xV_2O_5 \quad (1)$$

Whittingham et al. have presented comprehensive reviews on lithium battery cathode materials including lithium metal oxides and vanadium oxides.33,34 For Li-ion intercalation applications, vanadium pentoxide offers the essential advantages of low cost, abundant source, easy synthesis, and high energy densities.

In addition to crystalline $V_2O_5$, rather promising results have been reported for hydrated vanadium pentoxide ($V_2O_5 \cdot nH_2O$), such as $V_2O_5 \cdot nH_2O$ glasses with $P_2O_5$ or other network formers.35 $V_2O_5 \cdot nH_2O$ aerogels,36,37 and $V_2O_5 \cdot nH_2O$ xerogels.38 Specific energies of over 700 W h/kg were measured for lithium cells with a xerogel positive electrode.37 $V_2O_5 \cdot nH_2O$ xerogels are composed of ribbonlike particles and display lamellae ordering, with water molecules intercalated between the layers.39 These water molecules expand the distance between the layers, and the intercalation capacities of $V_2O_5 \cdot nH_2O$ xerogels are enhanced as a result.37 However, the intercalation capacity and charge/discharge rate of $V_2O_5$ are limited by the moderate electrical conductivity ($10^{-5} \rightarrow 10^{-3}$ S/cm)20,40 of $V_2O_5$ and the low diffusion coefficient of Li ions ($10^{-12} \rightarrow 10^{-13}$ cm$^2$/s)$^{41,42}$ in the $V_2O_5$ matrix.

Many studies have been conducted to improve lithium diffusion and electrical conduction performance in $V_2O_5$ by crystal structure modification toward a more open structure and by coating of $V_2O_5$ on highly conductive materials.43 Other approaches include making use of nanostructured materials that possess large surface area and short diffusion paths.

In this paper, the aspect of nanostructured vanadium pentoxide used in electrochemical energy storage will be addressed in detail, whereas we will also touch on the utilization of nanostructured $V_2O_5$ in other nanodevices such as sensors, actuators, and transistors. Selected recent examples from our laboratory and other research groups illustrate the synthesis and characterizations of a large variety of one-dimensional nanostructured $V_2O_5$, including nanowires45–48 nanobelts,31 nanorolls,49 ordered arrays of nanorods,50–52 nanotubes,53 and nanocables.54 It is the uncomplicated sol–gel processing (soft chemistry) method in combination with template synthesis or hydrothermal treatment that produces the most desirable nanostructures with remarkable reliability, efficiency, selectivity, and variety. Further, without any external effort, negatively charged nanowires of vanadium pentoxide can grow spontaneously in the sol. Other fabrication methods of vanadium pentoxide nanostructures include the reverse micelle technique, and the size of the nanorods of $V_2O_5$ can be tuned easily by keeping the freshly made nanorods in the micellar solution.55 Whittingham’s group recently reported another new method to produce vanadium oxide nanofibers with dimensions less than 140 nm by coating vanadium oxide on polylactide fibers.56 Electrochemical studies reveal that these vanadium oxide nanofibers are redox active and readily undergo reversible reactions with lithium ions.

### 2. Structures and Properties of Vanadium Oxides

Like most transitional metals, vanadium can exist in different valence states and consequently form a variety of oxides including VO, $V_2O_3$, VO$_2$, and $V_2O_5$. Figure 1 presents the partial phase diagram of the V–O binary system.57 In addition to these simple oxides, there are many other closely related structures where vanadium atoms have different valences between $V_2O_3$ (+3) and VO$_2$ (+4) and between VO$_2$ (+4) and $V_2O_5$ (+5). The series $V_nO_{2n-1}$ (1 < $n$ < 9) between VO$_2$ and VO$_3$, as well as $V_2O_3$, $V_3O_9$, $V_6O_{13}$, and $V_3O_7$ have all been observed.58 Hence, the phase equilibria in the vanadium–oxygen system are rather complicated.59 Vanadium oxides display a complex structural chemistry. For example, VO$_2$ exhibits a rutile structure while VO$_2$·0.5H$_2$O has a layer structure.60 The structure of $V_2O_5$ exhibits characteristic features of two-dimensional vanadium oxides.61 Mixed valence materials of V (+4)/V (+5) show a particularly rich crystal chemistry. The detailed and useful structural classification of various vanadium oxides can be found in a review by Zavalij and Whittingham.62 Among vanadium oxides, only $V_2O_5$ and $V_6O_{13}$ have gained importance as intercalation materials.
Orthorhombic crystalline V$_2$O$_5$ consists of layers of VO$_5$ square pyramids that share edges and corners. The apical V–O bond distance is much shorter than the four other distances and corresponds to a double bond. The layered structure of V$_2$O$_5$ illustrates a two-dimensional character for this material; however, the structure of V$_2$O$_5$ can be described as distorted VO$_6$ octahedral as well. The structural anisotropy of this material is illustrated by the very large length of the sixth V–O bond which gives rise to the ability to insert guest species in perovskite-like cavities.

Low-crystalline hydrated vanadium pentoxide (V$_2$O$_5$·nH$_2$O) is another Li-ion intercalation material, but its crystal structure has not been solved until recently. Petkov et al. have recently determined the full three-dimensional structure of V$_2$O$_5$·nH$_2$O using the atomic pair distribution function (PDF) technique, which is particularly powerful for structural characterization of crystalline materials with significant intrinsic disorder. This technique takes both the Bragg as well as the diffuse component of the diffraction data into account and thus yields structure parameters reflecting both the long-range order and the local structural disorder in materials. The structure of the V$_2$O$_5$·nH$_2$O xerogel can be visualized as an assembly of well-defined bilayers of single V$_2$O$_5$ layers made of square pyramidal VO$_5$ units with water molecules residing between them. This structure possesses enough atomic ordering perhaps to be characterized as nanocrystalline. As summarized earlier, crystalline V$_2$O$_5$ is an ordered assembly of single layers of V$_2$O$_5$. The V$_2$O$_5$·nH$_2$O xerogel is a stack of well-organized slabs which are bilayers of single V$_2$O$_5$ layers made up of square pyramidal VO$_5$ units, as shown in Figure 3a. The closest distance between the bilayers is about 11.5 Å. When the xerogel intercalates or extracts guest species, this distance expands or contracts correspondingly. The distance between the two single sheets of V$_2$O$_5$ making up the bilayer slab is approximately 2.90 Å. The coordination environment of V atoms in each bilayered slab can be taken as octahedral. The VO$_5$ octahedra share edges to from double chains propagating down the b axis. These double chains then arrange in parallel and side by side via interchain V–O bonds by sharing corners of octahedra to form the slab. Similarly, crystalline V$_2$O$_5$ consists of monolayered slabs composed of parallel double chains, on the basis of such one-dimensional chain-based slab structure, needlelike crystal growth appears in crystalline V$_2$O$_5$ and long nanoribbons are formed in the V$_2$O$_5$·nH$_2$O xerogels. Figure 3b shows the thermogravimetric trace for V$_2$O$_5$·nH$_2$O xerogels. It reveals the existence of 1.6 mol of water per mole of oxide at room temperature (assuming V$_2$O$_5$ as the solid phase after heating at >330 °C, whereas water is the only volatile phase in the initial film). The weight change profile for the xerogel is characterized by a steep loss between room temperature and 100 °C, followed by a more gradual weight loss up until 330 °C. Thermal treatment at 110 °C produced a xerogel with the V$_2$O$_5$·0.6H$_2$O composition. Continued heating to 250 °C produced V$_2$O$_5$·0.3H$_2$O by removing bound water. Heating above 300 °C induced loss of tightly bound water and crystallization of material, as discussed in the X-ray diffraction (XRD) results. For V$_2$O$_5$·nH$_2$O, the interlayer spacing $d$ can be calculated from the diffraction angle of the (001) peak. Figure 3c summarizes the dependences of interlayer spacing on the n value in V$_2$O$_5$·nH$_2$O. For samples treated at 25, 110, and 250 °C, the interlayer spacings show a slight decrease from 11.74 to 11.15 Å as the temperature goes higher; however, the change is rather small and the results are consistent with the 11.5 Å reported in previous reports. For the sample annealed at 300 °C in which low-crystalline V$_2$O$_5$·nH$_2$O coexists with orthorhombic V$_2$O$_5$, the interlayer spacing of V$_2$O$_5$·nH$_2$O is 8.43 Å, apparently smaller than the samples treated from 25 to 250 °C. Thermogravimetric analysis (TGA) results have shown that 110 °C corresponds to V$_2$O$_5$·0.6H$_2$O and 250 °C corresponds to V$_2$O$_5$·0.3H$_2$O. It can be concluded that interlayer spacings do not change much when only bound water (reversibly absorbed or hydrogen-bonded water) is removed. These parameters will alter considerably only when tightly bound (chemically bonded) water is removed and the material is on the verge of crystallization.

Vanadium pentoxide can intercalate a large variety of molecules and ions. The intercalation of organic molecules by V$_2$O$_5$ can be found in a review by Hagrman et al. The Ag or Cu doped vanadium pentoxide xerogels can function as high capacity (500–500 mA h/g) and high-energy cathode materials in lithium batteries. Vanadium oxides that contain Ag or Cu are particularly interesting because Ag or Cu ions can be exuded from the lattice increasing the electronic conductivity of the cathode material. The compound Ag$_2$V$_4$O$_11$ has been commercially used as the cathode material for the power source in medical devices. Another compound Cu$_{2.33}$V$_4$O$_{11}$ has attracted much attention and has been reported to be more rechargeable than the silver vanadium oxide. Electro-oxidation of Cu$_{2.33}$V$_4$O$_{11}$ yields a new compound Cu$_{1.1}$V$_{0.7}$O$_{11}$ which exhibits enhanced cycling performance with a capacity of about 200 mA h/g at the current densities from 0.1 to 1 mA cm$^{-2}$ over the first 20 cycles.

The reversible electrochemical lithium intercalation into V$_2$O$_5$ at room temperature was first reported by Whittingham in 1975. Afterward several phases were observed depending on the amount of inserted lithium: α and ε phases exist for $x < 0.01$ and $0.35 < x < 0.7$ in Li$_x$V$_2$O$_5$, respectively,
showing a V$_2$O$_5$-type structure with increasing puckering of the layers.$^{79}$ The composition LiV$_2$O$_5$ corresponds to the $\delta$ phase formed by gliding of one layer out of two.$^{80}$ For $x \leq 1$, the original V$_2$O$_5$ structure can be recovered upon lithium deintercalation and the phase transitions are fully reversible.$^{81}$ However, for further lithium intercalation ($x > 1$), a reconstruction mechanism leads to the irreversible transformation from the $\delta$ phase to the $\gamma$-phase.$^{79}$ This $\gamma$-phase can be reversibly cycled in the stoichiometric range $0 < x < 2$ without changing the $\gamma$-type structure.$^{82,83}$ Upon further intercalation of a third lithium, the $\gamma$-phase will be irreversibly transformed to the $\omega$-phase with a rock-salt type structure. This $\omega$-phase can be prepared either electrochemically at a potential of about 1.2 V versus Li/Li$^+$ or chemically using an excess of butyllithium.$^{84,85}$ Almost all the lithium from the $\omega$-phase can be electrochemically deintercalated again. The resulted compound demonstrated a specific energy of up to 900 W-h/kg and 100 cycles with more than 450 W-h/kg cell in a voltage range between 3.4 and 1.9 V and thus showed great potential as a positive electrode material for secondary lithium batteries, which has been demonstrated for a $\omega$-Li$_x$V$_2$O$_5$/Li.$^{86}$ Figure 4 presents the evolution of Li$_x$V$_2$O$_5$ phases as lithium is intercalated into V$_2$O$_5$ and the cycling of the $\omega$-phase.$^{87}$ Hydrated vanadium pentoxide (V$_2$O$_5$·$n$H$_2$O) has also been widely studied for lithium ion applications. These low-crystalline materials have morphologies significantly different from those of crystalline V$_2$O$_5$ and offer essential advantages of a large electrochemically active surface area, small particle size, and low density. These characteristics provide both high overall diffusion coefficients and low volume expansion during lithium intercalation. However, limited long-term cycling stability is a major challenge of such electrode materials at present. Zakharova and Volkov,$^{88}$ and Dong et al.$^{89}$ have summarized the Li-ion intercalation properties of V$_2$O$_5$·$n$H$_2$O xerogels and aerogels, respectively.

### 3. Synthesis of Vanadium Oxide Nanostructures

Vanadium pentoxide gels can be easily synthesized from both inorganic and metal–organic precursors and remain stable for years. Sol–gel processing is the major method that has been used to prepare this gel. Many synthesis methods of vanadium pentoxide sols or gels have already been described in the literature. Ditte reported the first one in 1885 by heating ammonium vanadate in a platinum crucible, followed by reaction with hot nitric acid and mixing into water, which produced a red sol.$^{90}$ A similar synthetic procedure by using hydrochloric acid was reported later.$^{91}$ Aqueous solutions of VOCl$_3$ were later discovered to yield V$_2$O$_5$ sols through the thermohydrolysis.$^{92}$ The alcoholic sol—
gel routes employing hydrolysis and condensation of vanadium alkoxides VO(OR)₃ (R = alkyl chain) have been used since the beginning of the century. In addition to organic precursors, inorganic oxides can directly produce vanadium pentoxide gels as well. For example, a red aqueous sol of vanadium pentoxide can be achieved by reacting hydrogen peroxide with crystalline V₂O₅ powders. Even more simply, vanadium pentoxide gels can be obtained by melting the oxide heated around 800 °C followed by pouring into water, which facilitates large-scale production in industry. Moreover, vanadium pentoxide gels were found to be formed from hydration of amorphous V₂O₅. The amorphous oxide was obtained by splat-cooling from the melt, vapor deposition, or O₂−H₂ flame fusion. Gels or colloidal solutions are resulted from dissolving these oxides into water. This hydration process was described as the swelling of a polymeric network into the solvent. Hydration seems to be characteristic of the amorphous state.

Recent sol−gel syntheses of vanadium pentoxide gels are grouped into three convenient routes: (1) acidification of NaVO₃ using an ion-exchange process and polymerization of the resultant HVO₃ in water, (2) hydrolysis and condensation of vanadium alkoxide, and (3) reaction between H₂O₂ and V₂O₅ powder. Synthesis of V₂O₅ has been dominated by the NaVO₃ route, and detailed research has been done on both the NaVO₃ route and the V alkoxide route to investigate the reaction mechanisms. For example, Holland et al. have recently compared thermal behavior and Li⁺ diffusion constants in V₂O₅+nH₂O xerogels prepared from the NaVO₃ and V alkoxide routes. Their report revealed that the V₂O₅+nH₂O xerogels made from these two methods have significant differences besides many similarities. Although the NaVO₃ route is the most commonly used and the V alkoxide route has been used increasingly, these two methods suffer from a few disadvantages. The NaVO₃ route may introduce contamination of sodium ions, and the concentration of vanadium is subject to change because of the additional water in the resin during the ion-exchange process. The ion-exchange process also causes a difficulty for large-scale production. In the V alkoxide route, the high reactivity of the alkoxide and its dependence on pH, temperature, and reactant concentrations make the chemical synthesis of V₂O₅+nH₂O gels rather delicate and difficult. A complexing agent such as acetic acid or acetyl acetone can be added to control the reaction rate; however, these agents also introduce complicated chemistry and the resultant sol may undergo slow side reactions for a long time. Therefore, the simple and clean H₂O₂−V₂O₅ route has attracted more and more attention recently. This method excludes the presence of foreign ions or organic ligands and offers precise control of vanadium concentration. The synthetic pathway and gelation process of the H₂O₂−V₂O₅ route have been studied by ⁵¹V NMR and laser Raman spectroscopic techniques lately. Our group has specifically utilized this method to obtain a stable V₂O₅+nH₂O sol which can be used in various deposition processes including electrophoretic deposition. Comprehensive reviews on synthesis and properties of vanadium pentoxide gels can be referred to Livage’s two articles. The orthorhombic phase of crystalline V₂O₅ is usually obtained by heating vanadium pentoxide gels above 350 °C in air.

This section reviews the major methods, that is, template synthesis and hydrothermal synthesis, that have been used to synthesize the various nanostructures of vanadium oxides in the present paper. Among many methods for the fabrication of nanomaterials ranging from physical techniques to chemical methods, template synthesis is one of the most important methods for synthesizing one-dimensional nanostructures. This process involves synthesizing a desired material within the pores of a porous membrane. A nanocylinder of the desired material is obtained in each pore because the membranes that are used have cylindrical pores of uniform diameter. The nanocylinder can be solid to yield a nanorod or hollow to yield a nanotube, depending on the properties of the material and the chemistry of the pore wall. Template membranes are track-etched polycarbonate (PC) membranes and anodic alumina membranes sold by a number of companies such as Millipore. The most straightforward and versatile template synthesis of nanostructures is template filling. Either a melt or a liquid precursor can be used to fill the pores. There are several concerns in the template filling. First, the wetability of the pore wall should be good enough to permit the penetration and complete filling of the liquid precursor or precursor mixture. For filling at low temperatures, the surface of pore walls can be easily modified to be either hydrophilic or hydrophobic by introducing a monolayer of organic molecules. Second, the template materials should be chemically inert. Third, control of shrinkage during solidification is required. If adhesion between the pore walls and the filling material is weak or solidification starts at the center, from one end of the pore, or uniformly, solid nanorods are most likely to form. However, if the adhesion is very strong or the solidification starts at the interfaces and proceeds inwardly, it is most likely to form hollow nanotubes. Electrochemical deposition is also called electrodeposition, a process involving electrochemical reaction that results in the deposition of solid material on an electrode. Nanocomposites are produced when the deposition is confined inside the pores of template membranes. Nanorods or nanotubes subsequently result when the template membrane is removed. During the electrodeposition, the electrode is separated from the depositing solution by the deposit after the initial deposition, and the electrical current must go through the deposit to allow the deposition process to continue. Therefore, electrochemical deposition is only applicable to electrical conductive materials such as metals, alloys, semiconductors, and electrical conductive polymers. Thus, the nanomaterials produced by template electrodeposition are mostly metals, chalcogenide semiconductors, and conducting polymers. Rarely can oxides be synthesized by this process, although a few semiconducting oxide nanostructures have been formed through conventional or novel electrochemical processes. The template-based electrodeposition process starts with coating one face of the membrane with a thin noble metal film via either ion sputtering or thermal evaporation. Thus, the coated membrane is then used as an electrode for electroplating. A general review on template synthesis can be found in Hulteen and Martin’s article. Finally, the template method can be...
combined with electrophoretic deposition. The major difference between electrophoretic deposition and electrochemical deposition is that the material deposited by electrophoretic deposition need not be electrically conductive. Electrophoretic deposition simply uses such an oriented motion of charged particles to grow films or monoliths by enriching the solid particles from a colloidal dispersion or a sol onto the surface of an electrode. At the beginning of the nanostructure growth, charged sol particles move as a result of electrophoresis toward the negative electrode. They deposit at the bottom of the pore, while the oppositely charged counterions move in the opposite direction. As time increases, the densely packed sol particles fill more of the pore, until the pore is completely filled. Fundamentals and practical approaches in growing oxide nanorod arrays through sol–gel processing and template-based electrophoretic deposition can be found in our published feature article.107

Hydrothermal synthesis is another powerful processes employed in nanochemistry. Especially when exposed to supercritical conditions, many starting materials undergo quite unexpected reactions that are often accompanied by the formation of nanoscopic morphologies, which are not accessible by classical routes. Another benefit from hydrothermal synthesis is the wide variety of parameters that can be chosen and combined: reaction temperatures close to room temperature or above 100 °C, variations in the pH value of the systems, concentration of solvents, introduction and removal of templates and other additives, choice of different autoclave geometries, and so forth.108 Combinatorial methods might be a suitable approach toward systematization of these parameter fields, but the problem of subsequent scale-up procedures always remains to be solved after a breakthrough in hydrothermal combinatorial synthesis. If, however, a standard procedure for hydrothermal formation of nanoparticles has been established, then these hydrothermal reactions are outstandingly efficient (almost 100% conversion of the starting material), time-saving, and experimentally effortless, such as the low-cost synthesis of vanadium oxide nanotubes.109 When planning a hydrothermal synthesis of nanostructures with a distinct anisotropic morphology, it is always convenient to start from an educt with a layered structure, especially when a template is involved.

4. Nanostructures of Vanadium Oxides with Enhanced Intercalation Properties

4.1. Nanorod Arrays of Polycrystalline Vanadium Oxide. Patrissi and Martin have used the template synthesis method to prepare nanostructured electrodes of orthorhombic V2O5 and have studied the effects of Li-ion diffusion distance and surface area on V2O5 rate capability.114 Nanorod arrays of polycrystalline V2O5 were prepared by depositing triisopropoxyvanadium(V) oxide (TIVO) into the pores of microporous PC filtration membranes. TIVO then underwent hydrolysis in the glovebox and condensation in an oxygen atmosphere, followed by sintering at 400 °C. The resultant sample is an ordered array of V2O5 which protruded from a V2O5 surface layer like the bristles of a brush. Figure 5 shows such nanorod arrays with various diameters and the PC filtration membranes. For nanorods that have the diameter of 115 nm and the length of 2 mm, the galvanostatic discharge performance of such nanostructured V2O5 electrodes was compared to a thin-film electrode of similar V2O5 mass and geometric area. Although the Li+ storage capacity of the thin-film electrode was equivalent to that of the nanostructured electrode at low (C/20) discharge rates, the nanostructured electrode demonstrated higher capacity than the film electrode at the high discharge rate. For example, the nanostructured electrode delivered three times the capacity of the thin film electrode at a rate of 200C; above 500C the nanostructured electrode delivered four times the capacity of the thin-film control electrode.

There have been intensive studies on applying nanotechnology into Li-ion battery design, and most of them are focused on the room-temperature performance.110–114 Li-ion batteries are efficient, lightweight, and rechargeable power sources for consumer electronics. However, the poor low-temperature performance of Li-ion batteries precludes the utilization of these batteries in a number of defense, space, and terrestrial applications.115 The amount of charge delivered from the battery at temperatures below 0 °C is substantially lower than the amount of charge delivered at room temperature.116–118 Li-ion battery electrodes composed of nanosized material may counter this low-temperature performance challenge, because nanomaterials can palliate the slow electrochemical kinetics problem and the slow diffusion problem by offering high surface area and short diffusion distance. Sides and Martin have demonstrated this case by showing that nanorods (diameter = 70 nm) of the electrode material V2O5 deliver dramatically higher specific discharge capacities at low temperature than V2O5 rods with micrometer-sized diameters.119 The template synthesis method was used to prepare cathodes composed of V2O5 nanorods or microrods with various diameters: 70 nm, 0.8 μm, and 0.45 μm as shown in Figure 5. The charge/discharge reactions and performance of these electrode materials were then investigated at different temperatures: 25, 0, and −20 °C. The template method allows the surface area of the electrode to be calculated from the fiber diameter, length, and pore density of the template membrane. The calculations show that 0.45 μm has the highest surface area, and the 0.8 μm
electrode has the lowest; the surface area of the 70 nm electrode is in between. However, it was found 70-nm-diameter nanorod arrays had the best low-temperature performance among the three, and the result is ascribed to its nanoscale (below 100 nm) and short diffusion distance. The poor low-temperature performance of Li-ion batteries is either due to a decrease in the diffusion coefficient within the electrode particles or due to a decrease in the rate of the electrode reactions with decreasing temperature. The experimental results of the 70 nm electrode having the best low-temperature performance show that temperature dependence of the solid-state diffusion coefficient determines the low-temperature performance of the electrodes.

For a large variety of Li-ion battery electrode materials, significant improvements in rate capabilities have been observed for the template-prepared nanostructured electrodes. Furthermore, a high volumetric energy density for the electrode is desired, because reduction in the size of consumer electronic devices has made the size reduction of Li-ion batteries necessary. PC membranes and alumina membranes are the two templates commonly used in preparing nanostructured electrodes. Alumina membranes have much higher porosity than PC membranes. However, removal of alumina membranes is accomplished by dissolving the membranes in acidic or basic solutions. Unfortunately, most electrode materials are oxides that are also soluble in these solutions, and the nanorod arrays will be dissolved along with the alumina templates. Therefore, a PC template is the remaining choice. The porosities of the PC membranes are rather low, for example, 1.2% for membranes that have 50-nm-diameter pores. Accordingly, this low porosity limits the number of nanorods of the electrode material and the resultant volumetric energy density of the nanostructured electrode.

Li and Martin have recently achieved improved volumetric energy densities of nanostructured electrode materials by chemically etching the PC membrane to increase its porosity prior to template synthesis. Figure 6 shows the scanning electron microscopy (SEM) image (top view) of the nanostructured V₂O₅ cathodes prepared from such an etched PC template. The pore diameter prior to etching is 50 nm. Such a nanostructured electrode is denoted as NSE. Furthermore, for some nanostructured electrodes obtained from etched templates, additional sol−gel precursor material was applied to the surfaces after template synthesis and removal of the etched membrane to further enhance the volumetric energy density. The resultant electrode is labeled as NSE+.

The rate capabilities of the NSE and NSE+ are compared to that of the thin film control electrode (shorted as TFE). Figure 7 summarizes the volumetric discharge capacities of these three typical electrodes as a function of discharge rate. At high discharge rate, both NSE+ and NSE electrodes have higher volumetric capacity than the TFE electrode, and NSE+ has the highest. At a lower discharge rate, the NSE+ electrode still has higher volumetric capacity than the TFE electrode. These results unambiguously demonstrate that template synthesis can be utilized to prepare nanostructured electrodes with good rate performance and high volumetric energy densities.

### 4.2. Nanorod Arrays of Single-Crystalline Vanadium Oxide

The advantage of template-based growth methods is the ability of fabricating unidirectionally aligned and uniformly sized nanorod arrays of a variety of materials. However, such methods suffer from inherent limitations. In particular, nanorods or nanowires synthesized by template-based growth methods are commonly either amorphous or polycrystalline and porous, which limits further studies on microstructure, properties and applications of such grown nanorods or nanowires. In addition, postdeposition annealing at elevated temperatures is often required to achieve desired density and mechanical integrity. Poor mechanical integrity and postdeposition annealing often result in break, distortion, and agglomeration of grown nanorods. Further study and development of template-based growth of single-crystal nanorods are obviously of significant importance; however, very limited research has been reported in the literature so far.

Single-crystal vanadium pentoxide nanorod arrays have been grown inside PC templates with the assistance of electric field from three different types of solutions or sol. Table 1 summarizes the growth conditions and shrinkage of V₂O₅ nanorod arrays grown from three different solutions or sols, that is, VO²⁺ solution (route A), VO₂⁺ solution (route B), and VO₂⁺ solution (route C).
B), and V₂O₅ sol (route C). It is noticed that under otherwise comparable growth conditions, nanorods grown by electrochemical deposition had a negligible shrinkage, whereas those grown through the change of pH value showed a noticeable 15% lateral shrinkage; moreover, nanorods from sol electrophoretic deposition had a substantial lateral shrinkage of 50%. Such a significant difference in lateral shrinkage of three nanorods upon firing can be explained by their distinctively different growth mechanisms.

Figure 8 shows SEM images of V₂O₅ nanorod arrays grown in 200 nm PC membranes and fired at 485 °C for 1 h in air from three different solutions and sols by either electrochemical or electrophoretic deposition. The images show that these nanorods are arranged almost parallel to one another over a broad area; the distortion is ascribed to the deformation of PC membrane during pyrolysis. There is negligible shrinkage along the long axis, but the morphology and diameter of nanorods grown from different solutions or sol are different. Nanorods grown from A and B solutions have a uniform diameter throughout their entire length with a smooth surface, but in the case of C, nanorods have a narrower diameter and slightly rough surface. XRD patterns (not shown here) reveal that all nanorod arrays have the same crystal structure, vanadium pentoxide, after firing at 485 °C regardless of the growth methods and the initial solutions.

Figure 9 presents typical transmission electron microscopy (TEM) micrographs and selected-area electron diffraction patterns (SAED) of V₂O₅ nanorods grown from electrochemical deposition (route A) and sol electrophoretic deposition (route C), respectively. No appreciable difference among nanorods grown by three different methods was observed. Figure 9a,c shows TEM images of a V₂O₅ nanorod and SAED pattern, which clearly demonstrated the single-crystalline nature or, at least, well-textured nature of the grown nanorods with a [010] growth direction for nanorods grown from both routes. Figure 9b,d also shows high-resolution TEM images of a single V₂O₅ nanorod, in which lattice fringes are clearly visible. The spacing of the fringes was measured to be 0.207 nm from route A and 0.208 nm for the nanorod from route C. These values are similar for different synthesis routes and correspond well with the spacing of the (202) planes at 0.204 nm. These fringes make an angle of 88.9° with the long axis of the nanorod, which is consistent with a growth direction of [010]. Similar measurements made on high-resolution images of other nanorods also yield results consistent with a [010] growth direction. Nanorods with the same orientation are grown from both solutions and the sol, but the formation mechanism of the single crystal is different. The formation of single-crystal nanorods from solutions, by both electrochemical deposition (route A) and pH-change-induced surface condensation (route B), is attributed to evolution selection growth as shown in Figure 10a. The initial heterogeneous nucleation or deposition on the substrate surface results in the formation of nuclei with random orientation. The subsequent growth of various facets of a
nucleus is dependent on the surface energy and varies significantly from one facet to another.\textsuperscript{133} In the case of nanorods made from the sol by electrophoretic deposition (route C), the formation of single-crystal V\textsubscript{2}O\textsubscript{5} nanorods is explained by so-called homoepitaxial aggregation of crystalline nanoparticles as shown in Figure 10b. Thermodynamically it is favorable for the crystalline nanoparticles to aggregate epitaxially; such a growth behavior and mechanism have been well-reported in the literature.\textsuperscript{134,135}

Figure 11 shows typical cyclic voltammograms (CVs) of V\textsubscript{2}O\textsubscript{5} nanorod arrays and the sol–gel film measured using a scan rate of 1 mV/s. Nanorod (a) from VOSO\textsubscript{4}, (b) from pH induced, and (c) from sol–gel electrophoresis and (d) the sol–gel film. (Reprinted with permission from ref 51. Copyright 2005 The Institute of Pure and Applied Physics.)

peak at 0.0 V, another anodic peak at −0.7 V is apparently observed; further, the cathodic peaks at −0.3 and −1.1 V are less distinct. The integrated areas of the CV curves for the nanorod array and sol–gel film are similar, which implies that both nanorod arrays and films possess the same specific energy at this scan rate. However, extraction and intercalation kinetics are different as evidenced by the sharp peaks from the solution route as compared to far less distinctive peaks in the CV curve of the sol–gel film. The behavior of the CV curve of the nanorod array made from the sol (route C) is between that of the nanorod arrays grown from solutions (route A and B) and that of the sol–gel film, although the nanorods made from all three routes are single-crystalline.

Figure 12 shows the comparison between the current density and Li\textsuperscript{+} intercalation capacity of nanorod arrays and sol–gel films measured by chronopotentiograms (CPs). In general, for a given Li\textsuperscript{+} intercalation capacity, for example, Li_{0.7}V\textsubscript{2}O\textsubscript{5}, nanorod arrays from solution route possess an up to five times larger current density than that of sol–gel films, which is larger than that of the sol electrophoresis nanorod. Similarly for a given current density, such as 0.7 A/g, nanorod arrays can store up to five times more Li than in sol–gel films and more than in the sol electrophoresis nanorod. The differences in electrochemical properties observed in vanadium pentoxide nanorod arrays and films are attributed to the differences in microstructure and nanostructure. V\textsubscript{2}O\textsubscript{5} nanorods grown by electrophoretic deposition from solutions (route A and B) are dense single crystals, with layers parallel to the nanorod axis. Such a structure is extremely favorable to Li\textsuperscript{+} intercalation and extraction, because the surface oxidation and reduction reactions occur along the surface of the nanorods and the solid-state diffusion distance is very small, ~100 nm, half of the diameter of the nanorods. In addition, such structure permits the most freedom for dimensional change that accompanies intercalation and extraction reactions. Such well-aligned structure will also enhance the Li\textsuperscript{+} diffusion through the solvent. The nanorod grown from sol electro-
phoresis (route C) is also single-crystalline and well-aligned, but it has many defects inside the crystal. That may cause the difference between these nanorod array electrodes. Sol—gel derived V_2O_5 films are polycrystalline and consist of platelet V_2O_5 grains with [001] perpendicular to the substrate surface. Therefore, the Li^+ intercalation and extraction processes will comprise of Li^+ diffusion through grain boundaries, oxidation and reduction reactions at the surface of individual crystal grains, and diffusion inside individual grains. Thus the difference in microstructure will have similar effects on the kinetics charge transport.

V_2O_5 is also an electrochromic material that exhibits a reversible optical change between the transparent state and the colored state upon extraction and intercalation of lithium ions. Figure 13 shows the change of transmittance intensity at 700 nm as a function of time when an external voltage of 3.0 V is applied for the V_2O_5 nanorod array grown by electrophoretic deposition from the sol and the sol—gel derived V_2O_5 film, respectively. A 30% reduction was achieved in ~50 s in the V_2O_5 nanorod array; however, 300 s were required in the film. The transmittance change of the nanorod array reached saturation in 3 min, while the sol—gel derived film was not yet saturated in 5 min. Extrapolation from the data in Figure 13 suggests that the sol—gel film will require at least 10 min to reach the same saturation, that is, the sol—gel film has a three times slower responding speed than the nanorod array. In conclusion, both the extent and the speed of change in the transmittance intensity of the nanorod array are significantly faster than those of the sol—gel derived film, corroborating with an enhanced electrochemical intercalation process in nanorod arrays due to a large surface area for the surface redox reaction and a short and easy diffusion path for mass and charge transport.

4.3. Nanotube and Nanocable Arrays of Vanadium Oxide. Compared to nanorods, nanotubes possess several different areas of contact, that is, the inner and outer wall surfaces as well as the open ends. In principle, nanotube arrays have an even larger surface area than nanorod arrays. In addition, the tubes can operate as electrolyte-filled channels for faster transport of the ions to the intercalation sites. The first successful approach to make a tubular vanadium oxide was with the use of carbon nanotubes as a template. It was possible by exploitation of surface-tension effects to coat the carbon nanotubes externally with crystalline layers of a V_2O_5-like structure. We have also prepared nanotube arrays of V_2O_5·nH_2O through the template-based electrodeposition method from VO_3^− solution by using lower voltage and shorter deposition time compared to the conditions for preparing nanorod arrays. Figure 14 shows SEM images of the (a) top view and (b) side view of V_2O_5 nanotube arrays grown within the pores of the PC membrane after the membrane is dissolved away in methylene chloride. These nanotubes stand apart from each other and project straight up from the substrate surface, with a length of 10 μm (image not shown). As can be seen from the TEM images in Figure 14c, the outer diameter of the nanotube is about 200 nm and the inner diameter of the nanotube is about 100 nm. No electron diffraction pattern in TEM was observed, which suggests the amorphous nature of these nanotubes. XRD analysis of nanotube arrays shows its amorphous state as well. The possible mechanism of the nanotube growth is discussed as follows. A very thin coating of the Au—Pd alloy on the PC membrane results in a coating of metal on the edges of the pores, leading to high current density on these edges, where electrochemical reaction and deposition are initiated. On the edges of the pores, the ionic cluster, VO_3^+, is oxidized to deposit V_2O_5 through the following reaction:

\[
2\text{VO}^{2+} + 3\text{H}_2\text{O} \rightarrow V_2\text{O}_5 + 6\text{H}^+ + 2e^- \quad (2)
\]

Simultaneously a reduction reaction occurs at the counter electrode:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \quad (3)
\]

Figure 15a shows the first three voltammetric cycles of the V_2O_5·nH_2O nanotube arrays in the potential range between −1.6 and 0.4 V versus Ag/Ag^+ and using a scan
nH₂O itself prepared from electrochemical deposition has demonstrated an initial high capacity of 300 mA h/g by the nanotube array. However, the capacity of the nanotube array is lower than the stabilized capacity of V₂O₅. The capacity of both the nanotube array and the film prepared from the electrochemical deposition method. The capacity of the nanotube array is calculated from chronopotentiometric measurements at a 0.4 V to −1.5 V cutoff voltage vs Ag/Ag⁺. (Reprinted from ref 53. Copyright 2005 American Chemical Society.)

Figure 15. (a) CVs of the V₂O₅ nanotube array in a potential range of −1.6 to +0.4 V vs Ag/Ag⁺ and under the scan rate of 10 mV/s. Solid line, the first cycle; dashed line, the second cycle; and dotted line, the third cycle. (b) Dependence of the discharge capacity on the cycle number obtained from the electrochemical redox cycles, indicating the material loses some electroactivity. The degradation may be either ascribed to the electrochemically deposited V₂O₅·nH₂O itself or due to the fragile structure of the nanotubes. Consistent with CVs, CPs have shown that nanotube arrays exhibit degradation in electrochemical performance as well, and the quantitative results of the capacities calculated from chronopotentiometric measurements are discussed as follows. Figure 15b illustrates the dependence of the discharge capacity on the cycle number of both the nanotube array and the film prepared from the electrochemical deposition method. The capacity of the nanotube array is calculated on the basis of the outer diameter of 200 nm, the inner diameter of 100 nm, the length of 10 μm, and the density of 2.87 g/cm³. The V₂O₅·nH₂O nanotube arrays demonstrate an initial high capacity of 300 mA h/g, about twice the initial capacity of 140 mA h/g from the V₂O₅·nH₂O film. Such enhancement of capacity is due to the large surface area and short diffusion distances offered by the nanotube array. However, the capacity of the nanotube array decayed to 200 mA h/g in the second cycle and 180 mA h/g in the third one. The degradation is slower in the further cycles and finally reaches a stabilized capacity of 160 mA h/g after the sixth cycle which is about 30% higher than the stabilized capacity of the V₂O₅·nH₂O film. The initial degradation of the V₂O₅·nH₂O film suggests that V₂O₅·nH₂O itself prepared from electrochemical deposition has some drawback and suffers a slight loss of electroactivity during cycling. However, the nanotube array shows a more drastic decay of initial performance compared to the film during cycling, possibly due to the morphological flexibility and fragility of nanotubes, which has been speculated in the literature as well.⁴⁹

Further, a two-step electrodeposition method has been used to prepare Ni−V₂O₅·nH₂O core−shell nanocable arrays. Ni nanorod arrays were first grown by template-based electrochemical deposition. In the second step, the hydrated vanadium pentoxide shell was deposited onto the surface of nickel nanorods through sol electrophotoetric deposition.
for Ni–V₂O₃·nH₂O nanocable arrays, single-crystal V₂O₃ nanorod arrays, and V₂O₃ films. The intercalation capacities of both nanorod arrays and sol–gel films decrease rapidly as the current density increases, while nanocable arrays are able to retain the high intercalation capacity at high current density (discharge rate), indicating the excellent high-rate performance of nanocable arrays. Figure 17c shows that the Ni–V₂O₃·nH₂O nanocable array has significantly more enhanced energy density and power density than those of the nanorod array and sol–gel film by at least 1 order of magnitude.

4.4. Nanostructured Films of Vanadium Oxide with Various Features. Platelet and fibrillar structured V₂O₅ films have been prepared by solution methods, and the discharge capacities and cyclic performance of these films were compared with those of the conventional plain structured film. The platelet film consists of 20–30 nm sized V₂O₅ particles with random orientation, whereas fibrillar film is comprised of randomly oriented fibers though most of them protrude from the substrate surface. The initial discharge capacities of platelet and fibrillar structured V₂O₅ films are 1240 and 720 mA·h/g, respectively, which are far larger than the initial discharge value (260 mA·h/g) of the plain structure film. Such large discharge capacity values are ascribed to the combined effects of the reduced Li⁺ diffusion distance, which prevents concentration polarization of Li⁺ in the V₂O₅ electrode and poor interlayered cross-linking offering more Li⁺ intercalation. However, platelet and fibrillar structured V₂O₅ films were easily degraded during electrochemical cyclic tests. Figure 18 shows the SEM observation of the surface morphology of the resulting films. The V₂O₅ film made from the V₂O₅ sol (see Figure 18a) shows a typical smooth surface morphology with some voids throughout the film. The film prepared by using VOSO₅ shows a randomly oriented platelet-like morphology with most platelets standing almost vertically and commonly having a thickness of 20–30 nm as shown in Figure 18b. Figure 18c shows the film prepared using VO³⁺ solution, and the film shows an assembly of fibrillar particles of 20–40 nm in diameter protruding from the current collector surface like the bristles of a brush.

4.5. Nanorolls and Nanobelts of Vanadium Oxide. A fundamentally new type of vanadium oxide nanoroll was prepared in a sol–gel reaction of vanadium oxide precursor conducted in the presence of an amine and followed by hydrothermal treatment. The vanadium oxide precursor can be vanadium alkoxide or a low-cost source such as V₂O₅, VOCl₃, or HVO₃. The amine has long alkyl chains and functions as a molecular and structure directing template; typical templates are monoamines (C₆H₁₃NH₂ with 4 ≤ n ≤ 22) or diamines (H₃N(CH₂)₄NH₂ with 14 ≤ n ≤ 20), or even aromatic amine such as phenylpropylamine. The resultant material is black in color and easily available in high yield. There is a relatively large amount of organic template built into the oxide structure during hydrothermal synthesis, for example, VO₂.₄₅(TEMP)₀.₃₄ when the template (TEMP) is C₁₀H₁₅NH₂. There is a slight reduction of vanadium(V) during hydrothermal reaction, leading to a small fraction (~5%) of vanadium(IV) in addition to vanadium(V) in the material. Therefore, the material is represented by VOₓ (vanadium oxide).

As seen from the TEM image in Figure 19a, the VO₅ nanorolls with the composition of VO₂.₄₅(TEMP)₀.₃₄ (TEMP = C₁₀H₁₅NH₂) have open ends, consisting of several concentric shells, each about 2.8–3 nm in thickness. The nanoroll is either constructed in closed concentric cylinders (nanotubes) or formed by scrolling one or more layers (nanocylinders) as shown in Figure 19b. The outer diameters of the VO₅ nanorolls range from 15 to 150 nm, and lengths are in the range of 0.5–15 μm. It is interesting to note that nanorolls obtained with monoamines tend to form thin walls that comprise rather few layers (2–10), whereas diamines...
experimental evidence and structural simulation show that templates have no influence on the wall structure. All influenced by the template size, indicating that different composed of two sheets of VO\textsubscript{5} square pyramids connected about 0.62 nm. The positions of the indicating a two-dimensional square lattice with a length of NH\textsubscript{4}+ are located in the wide layers, and the comparatively smaller shown in Figure 20b. It is assumed that amine molecules consists of two different, alternating, interlayer distances as conventional nanotubes. The tube wall is relatively thin and of the tube is around 200 nm and is much larger than that cross-sectional TEM image of the nanotube. The diameter is first observed in a tubular phase. Figure 20a shows the alternating interlayer distances, and such a unique structure is structural breakdown during redox cycles and degradation in cycling performance due to the morphological flexibility. In most cases, VO\textsubscript{x} nanorolls show defects such as gaps in the VO\textsubscript{x} layers inside the walls. Sun et al. have recently investigated the relationship between the synthesis chemistry, the nanoscale structure, and the electrochemical performance of vanadium oxide nanorolls. The VO\textsubscript{x} nanorolls exhibit different morphologies and properties depending upon the synthetic conditions. Higher reducing conditions yield nearly perfect nanorolls showing no oxide cracks in the walls, whereas less reducing conditions produce defect-rich nanorolls with many cracks in the walls. Both types of nanorolls predominantly lead to nanorolls with relatively thick walls consisting of more than 10 layers. XRD patterns of VO\textsubscript{x} nanorolls show the highly intense and sharp 00l reflections at low scattering angles that are characteristic of a well-ordered layered structure. The interlayer distances of these reflections range from 1.7 to 3.8 nm and increase linearly with the size of the amine molecules. This indicates that protonated template molecules are embedded between the VO\textsubscript{x} layers, and interlayer distances between approximately 1.7 and 3.8 nm can be achieved in a controllable way. Less intense and broad hk0 reflection peaks appear at higher scattering angles in the XRD patterns of VO\textsubscript{x} nanorolls, indicating a two-dimensional square lattice with a length of about 0.62 nm. The positions of the hk0 peaks are not influenced by the template size, indicating that different templates have no influence on the wall structure. All experimental evidence and structural simulation show that the VO\textsubscript{x} layers have the composition V\textsubscript{7}O\textsubscript{16}. The layers are composed of two sheets of VO\textsubscript{5} square pyramids connected by VO\textsubscript{4} tetrahedra and pointing in the opposite direction.\textsuperscript{150,151} Pillai et al. have prepared a new type of vanadium oxide nanoroll (nanotube) by applying ammonia during the hydrolysis step of the synthesis.\textsuperscript{152} The resultant nanotubes have alternating interlayer distances, and such a unique structure is first observed in a tubular phase. Figure 20a shows the cross-sectional TEM image of the nanotube. The diameter of the tube is around 200 nm and is much larger than that conventional nanotubes. The tube wall is relatively thin and consists of two different, alternating, interlayer distances as shown in Figure 20b. It is assumed that amine molecules are located in the wide layers, and the comparatively smaller NH\textsubscript{4}+ ions are embedded in the narrow separation. The narrower interlayer distance makes the tube structure stiffer than that with only amine molecules. This stiffer structure makes rolling and bending difficult and thus results in the larger diameter of these tubes compared to the VO\textsubscript{x} nanorolls with evenly separated interlayers.

In comparison with other tubular systems, the VO\textsubscript{x} nanorolls are especially interesting because they possess four different contact regions, that is, tube opening, outer surface, inner surface, and interstitial region. Therefore, the VO\textsubscript{x} nanorolls are very promising for the realization of highly functional and effective nanodevices such as sensors, single-electron transistors, and energy storage/release systems. VO\textsubscript{x} nanorolls can intercalate a variety of molecules and ions reversibly without change in the crystalline structure. Various metal ions, for example, Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Fe\textsuperscript{2+}, or Co\textsuperscript{2+}, can be intercalated into VO\textsubscript{x} nanorolls to substitute the monoamine molecules embedded in the interlayer structure.\textsuperscript{153} Even diamines can be intercalated into the interlayer structure to replace the monoamines simply by mixing with a suspension of the VO\textsubscript{x} nanorolls.\textsuperscript{154} Intercalated monoamines can be substituted by diamines simply.\textsuperscript{154} More specifically, intercalation of lithium ions into VO\textsubscript{x} nanorolls have been studied intensely recently\textsuperscript{49,155,156} and opens up some new perspectives for battery applications. The discharge capacities have been found up to 200 mA-h/g; however, there is structural breakdown during redox cycles and degradation in cycling performance due to the morphological flexibility.

Figure 19. TEM images of (a) C\textsubscript{16}–VO\textsubscript{x} nanorolls. (b) Cross-sectional structure of C\textsubscript{6}–VO\textsubscript{x} nanorolls: the nanoroll on the left is nanotube composed of five concentric VO\textsubscript{x} layers, and that on the right is the nanoscroll with gaps at several sites in the layers. (Reprinted with permission from ref 49. Copyright 1999 Electrochemical Society.)

Figure 20. TEM images of VO\textsubscript{x} nanorolls with two different interlayer spacings (~0.9 nm and ~2.0 nm; template, dodecylamine): (a) cross-sectional structure of the tube showing the bending and (b) a closer look at the tube wall. (Reprinted with permission from ref 152. Copyright 2001 Elsevier.)
then undergo ion-exchange reactions to replace the templating ammonium ions with Na\(^+\), followed by electrochemical characterizations to examine the Li\(^+\)-intercalation performance. The cyclic voltammetry measurements show that the well-ordered nanorolls behave closely to classic crystalline vanadium pentoxide, while the defect-rich nanorolls have electrochemical behavior similar to that of sol–gel-prepared hydrated vanadium pentoxide materials whose crystalline order is restricted to nanoscale. The specific capacity of defect-rich nanorolls (340 mA·h/g) is higher than that of the well-ordered nanorolls (240 mA·h/g) under comparable conditions. Furthermore, the defect-rich nanorolls demonstrate better cycling performance. The enhanced capacity in defect-rich nanorolls is ascribed to the additional redox sites resulted from the nanoscale disorder. The cracks and shedding in the defect-rich nanorolls also lead to increased accessibility of lithium ions to the interlayer regions and thus result in the improved cycling performance. In conclusion, VO\(_2\) nanorolls may find a bright future as high-performance cathode materials by modifying the morphology and structure.

Owing to the layered structure, vanadium pentoxide and especially hydrated vanadium pentoxide that has larger interlayer spacing allow gas molecules to enter and approach the active position easily, thus finding applications as sensor materials. For example, alcohol gases containing hydroxyl groups can be adsorbed on V–O layers by hydrogen bonds and then react with the negative oxygen to change the conductivity of the sensors. Biomedical, chemical, and food industries have a strong demand on alcohol sensors with high conductivity of the sensors. Biomedical, chemical, and food industries have a strong demand on alcohol sensors with high selectivity and stability for breath analysis or wine-quality monitoring. Conventional ethanol sensors are mostly based on SnO\(_2\), ZnO, TiO\(_2\), and Fe\(_2\)O\(_3\) and usually suffer from cross-sensitivity to other gases, low long-term stability, a need for high working temperature, or a lack of high sensitivity to lower-level ethanol vapor.\(^{159}\) Therefore, some new types of ethanol-sensing materials are still being studied and developed. One-dimensional nanostructures of various metal oxides have been synthesized and investigated for gas sensors.\(^{160–163}\) Specifically, nanobelts of oxides are very promising for sensors due to the high surface-to-volume ratio and single-crystalline nature.\(^{164,165}\)

Pan et al. used a hydrothermal method to synthesize long beltlike nanowires, which are several tens of micrometers long and a few tens of nanometers wide, and are crystallized well growing along the [010] direction.\(^{166}\) A hydrothermal method was later used by Schlecht et al. to synthesize new types of vanadium oxide belts exhibiting a boomerang shape.\(^{167}\) A layered structure was revealed closely corresponding to that in known vanadium pentoxide nanofibers. The structure of nanobelts is unique in that it originates from twinning along the [130] direction, which is the first observation of twins within individual nanosized crystals. However, the intercalation properties of these beltlike nanowires or boomerang-shaped nanobelts of vanadium oxides are not further investigated. Liu et al. have recently synthesized vanadium pentoxide nanobelts for highly selective and stable ethanol sensor materials.\(^{21}\) The nanobelts were prepared by acidifying ammonium metavanadate followed by hydrother-
the selectivity of the vanadium pentoxide is also tested for practical purposes. It is found that the sensors are insensitive to CO and H₂ and the responses to H₂S, NH₃, H₂, C₃H₈, CO, and NOₓ are lower than the response to ethanol. It is expected that metal ion doping or organic template modification can further enhance the sensitivity of nanobelts of vanadium pentoxide as sensor materials.

4.6. Self-Assembly of Vanadium Oxide Nanowires. In addition to template synthesis and the hydrothermal route, one-dimensional nanostructures of vanadium pentoxide can grow spontaneously in the sol. The drawback of this method is that it takes a longer time; however, the V₂O₅ nanowires in the sol are negatively charged, and this property leads to novel processes of self-assembly and patterning for applications in nanodevices.

It has been known for a long time that colloids of vanadium pentoxide have the fibrous structure. Under an electric field or a shear stress, the V₂O₅ colloidal sols become anisotropic. V₂O₅ sols show amazing properties such as thixotropy and rheopexy and are often used as models to investigate the optical birefringence or the hydrodynamic behavior. In the sol made from vanadic acid aqueous solution, tiny threads of vanadium pentoxide about 2 nm wide and 100 nm long are formed first. These threads grow lengthwise, and the subsequent self-assembly edge-to-edge results in ribbonlike wires. Such growth can be explained by a condensation mechanism. Typically, gels of vanadium pentoxide are composed of ribbonlike nanowires about 10 nm wide and over 1 μm long.

Chang et al. recently reported growth conditions of V₂O₅ nanowires and demonstrated a simple but noble percolation system composed of the conducting nanowires and insulating matrix. V₂O₅ nanowires were prepared from ammonium (meta)vanadate and acidic ion-exchange resin. The length of V₂O₅ nanowires can be increased by polycondensation of vanadic acid in deionized water. As the reaction proceeded at room temperature, the lengths of the V₂O₅ nanowires increased at a speed of 0.13 μm/day at an early stage of the growth and 0.03 μm/day on the average up to 3 months. The percolation network was made by abruptly freezing the homogeneously dispersed aqueous solutions of V₂O₅ nanowires in liquid nitrogen. After 7 h of aging time, an abrupt increase of the conductance was observed, revealing the satisfaction of the percolation threshold \( P_c \sim 0.17 \) at the average wire length of 40 nm.

The idea of using V₂O₅ for converting electrical energy to mechanical energy has been considered for more than 10 years. This idea was first realized by Gu et al. who successfully prepared electrochemical actuators (artificial muscles) based on V₂O₅ nanowires. V₂O₅ nanowires were obtained from the sol synthesized by mixing ammonium meta-vanadate and acidic ion-exchange resin in water. The SiO₂/Si substrate was pretreated with (3-aminopropyl)-triethoxysilane (APTES) to generate positively charged ammonium groups on the surface to adsorb negatively charged V₂O₅ nanowires through ionic interaction. The resultant sample is an entangled network of V₂O₅ nanowires. Furthermore, free-standing sheets of V₂O₅ nanowires were prepared by filtering the sol of nanowires through a cellulose nitrate filter using a water aspirator. This procedure produced a brown sheet which was rinsed with water and then peeled off the filter paper, resulting in a free-standing sheet composed of entangled V₂O₅ nanowires. The nanowire sheet was heated at 80 °C to increase the flexibility and cause dehydration. The morphology of the resultant sheet looks similar to that of the sheet of single-walled carbon nanotubes used in the actuator. Electromechanical actuation was demonstrated for a V₂O₅ nanowire sheet immersed in an aqueous electrolyte. It was found that the V₂O₅ nanowire sheets provide a high Young’s modulus, high actuator-generated stress, and high actuator stroke at low applied voltage. Electrochemical charge injection and intercalation that causes the electromechanical actuation are made faster due to the high surface area of these V₂O₅ nanowire sheets. The actuation strain was observed to be 0.21%, and the force-generation capability was 5.9 MPa; additionally, the V₂O₅ nanowire sheets require much lower applied voltages than commercial ferroelectric and electrorheoactive materials. Thus, the V₂O₅ nanowire sheets open up a new perspective for redox-dependent application of V₂O₅ nanostructures as actuators.

Usually nanowires are synthesized in a solution or powder form. To build functional devices, individual nanowires have to be picked up and assembled onto the substrate, which cannot be achieved by conventional microfabrication strategies. However, the spontaneous growth of negatively charged V₂O₅ nanowires in the sol has stimulated some researchers to develop a simple and elegant method, the so-called “surface-programmed assembly” for high-precision assembly and alignment of pristine V₂O₅ nanowires on solid substrates. In this method, positively charged surface molecular patterns are used to assemble and align a large number of V₂O₅ nanowires over a large surface area, while neutral surface molecular patterns are used to prevent adsorption of nanowires. For example, self-assembled monolayer patterns of 1-octadecyltrichlorosilane (OTS) can be created on the surface of SiO₂ substrates with photolithography first to generate the neutral regions, and the remaining area is backfilled with APTES molecules to create positively charged areas. Negatively charged nanowires of V₂O₅ are attracted onto the positively charged APTES areas, and there is no nanowire on the OTS regions, as shown in Figure 22a. Furthermore, individual nanowires can be assembled using the same process. The length of V₂O₅ can be controlled by keeping the mixture of ammonium meta-vanadate and acidic ion-exchange resin for a certain time period. Longer aging time leads to longer V₂O₅ nanowires in the sol, for example, nanowires a few micrometers long are obtained by keeping the mixture for 20 days. Therefore, assembly and alignment of individual nanowires on the substrates can be achieved by placing the molecular patterns in the sol, as shown in Figure 22b.

The researchers further made a transistor device based on an array of nanowires by using the conventional lift-off method to fabricate Au electrodes on the nanowire array as shown in Figure 23. The observed gating effect is in good agreement with that reported in the literature, indicating...
more, purity of V2O5 nanowires is ensured because it is not external force for nanowire assembly or alignment. Furthermore, microfabrication processes and does not rely on any offers the capacity to be entirely compatible with conventional methods needed to chemically functionalize the nanowires. High-chemistry routes that involve sol-gel reactions and that frequently use organic molecules as structure-directing templates are simple and elegant. First, the template-based method has been utilized to prepare various ordered arrays of nanostructures, including polycrystalline V2O5 nanorod arrays, single-crystalline V2O5 nanorod arrays, V3O7·nH2O nanotube arrays, and Ni−V2O5·nH2O core−shell nanocable arrays. Morphology, structure, and growth mechanisms of these nanostructures have been discussed. The Li+−intercalation properties of the nanostructured electrodes have been compared to the film electrode of vanadium pentoxide. All nanostructured electrodes exhibit storage capacity and rate performance significantly improved over those of V2O5 films, as a result of the larger surface area and the shorter diffusion path. Moreover, the relationship between low-temperature performance of polycrystalline V2O5 nanorod arrays and the nanostructures is discussed, and the volumetric energy density of the V2O5 nanorod arrays can be improved by chemically etching the PC membranes prior to template synthesis. The hydrothermal route is another powerful tool for generalizing and systematizing controlled syntheses of nano-morphologies, such as VOx nanorolls for cathode materials in lithium ion batteries and V2O5 nanobelts for ethanol sensor materials. Negatively charged V2O5 nanowires can also grow spontaneously in a sol. This simple and controlled synthesis leads to easy fabrication of robust freestanding V2O5 nanowire sheets for actuation function, in addition to precise assembly and patterning of V2O5 nanowires for nanotransistor applications. Considering that vanadium oxides possess versatile redox-dependent properties, one can foresee the possibility of fabricating multifunctional and/or hybrid nanodevices based on it. Processing methods in this review are generally applicable to fabricating nanostructures of other oxides, for example, metal oxide core−shell nanocable arrays. Discussion on the underlying principle that affects the properties of V2O5 in the present work can be helpful for further understanding of vanadium oxide and other transition metal oxides.

5. Concluding remarks

Despite focusing on vanadium pentoxide, this review clearly reveals how moving from bulk materials to the nanoscale can significantly change their performance in devices for energy storage and conversion and for sensing and actuation. The development of nanodevices can benefit from the distinct morphology and high aspect ratio of one-dimensional anisotropic nanostructures as these can be functionalized in unique ways. Among a wide range of different synthetic methods to prepare nanomaterials, soft chemistry routes that involve sol−gel reactions and that

Figure 22. (a) Atomic force microscopy topography image of V2O5 nanowires assembled on APTES patterns on SiO2. OTS has been used for passivation. Insets show high-resolution atomic force microscopy images of the OTS (left) and APTES regions (right). (b) Atomic force microscopy topography image of individual V2O5 nanowires (white lines) assembled on cysteamine patterns (dark areas) on Au. ODT (1-octadecanethiol; bright areas) is used for passivation. (Reprinted with permission from ref 46. Copyright 2005 Wiley-VCH.)

Figure 23. Gating effect of V2O5 nanowire transistors. The n-type Si substrate is used as a back gate. The insets show optical micrograph images of Au electrodes and an atomic force microscopy topography image of nanowire patterns connecting those electrodes. (Reprinted with permission from ref 46. Copyright 2005 Wiley-VCH.)

that the device based on the V2O5 nanowire pattern functions properly.

This important “surface-programmed assembly” method offers the capacity to be entirely compatible with conventional microfabrication processes and does not rely on any external force for nanowire assembly or alignment. Furthermore, purity of V2O5 nanowires is ensured because it is not needed to chemically functionalize the nanowires. High-precision assembly and alignment of V2O5 nanowire arrays can be achieved over a large area of ~1 cm × 1 cm. Combination of the simplicity of this method and the versatile properties of V2O5 will lead to significant breakthrough toward sophisticated or multifunctional nanodevices.

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