A new solvo-hydrothermal method has been developed for the synthesis of uniform vanadium oxide nanocrystals (NCs) with various sizes and shapes in aliphatic amine/toluene/water using V(V) diperoxoid alkylammonium complexes. The vanadium complex precursors were prepared from an ion exchange reaction of V(V) diperoxidogels and tetraalkylammonium bromide in the water–toluene mixture using H₂O₂ solution and commercial bulk V₂O₅ powders as starting vanadium gel source. The obtained VO₂ NC products were characterized by means of transmission electron microscopy (TEM), selected area electron diffraction (SAED), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), Fourier transform infrared absorption spectroscopy (FTIR), thermogravimetric differential thermal analysis (TGA-DTA), and nitrogen adsorption/desorption (BET). The size and shape of NCs can be controlled by different synthesis parameters such as water content, steric ligands of complexes, alkyl chain lengths of capping aliphatic amines, as well as nature of solvent. Monodisperse vanadium oxide NCs with various sizes and shapes, nanospheres, nanocubes, nanorices, and nanorods, can be easily achieved. The possible mechanisms for the formation of vanadium complex precursors and vanadium oxide NCs as well as the shape evolution of NCs were also discussed. The as-made vanadium oxide products exhibited the monoclinic rutile VO₂ structure, which was however converted to the orthorhombic V₂O₄.₆ structure after calcination in air. The XPS results also revealed only one V⁴⁺ state for the as-made sample; however, the coexistence of V⁵⁺ and V⁶⁺ states and two components of oxygen associated with O=V and O–V for the calcined samples on the vanadium oxide NC surface were observed. The surface chemical composition of both as-made and calcined samples were found to be VO₂ and V₂O₅ₓ₋₆(x = 0.4), respectively. Our approach may provide a novel route for the extended synthesis to other inorganic NCs.

1. Introduction

Shape-selective synthesis of inorganic nanocrystals (NCs) is particularly attractive for exploring many of their unique material properties with respect to their bulk counterparts, since they are potential building blocks for catalysis, advanced materials, and optoelectronic devices.¹⁻⁶ For the past few years, various template-based methods including sol–gel,¹ thermohydrolysis of organometallics,⁸ reverse micelle technique,⁹ and solvo-hydrothermal treatment,¹⁰,¹¹ had been demonstrated a success in superior shape and size control. Among them, a solvothermal approach of decomposing metal complexes has been regarded as one of the most effective and economical routes,¹² as it has the merits of a single step low temperature synthesis.

Vanadium oxides (V₂O₅₋ₓ) are of interest due to their versatile redox activity and layered structures.¹³ They are a key technological material widely used in fields such as chemical sensing,¹⁴ actuators,¹⁵ high-energy lithium batteries,¹⁶ and electric field-effect transistors.¹⁷ In particular, V₂O₅₋ₓ NCs have high oxygen storage capacity (OSC) as a result of the multiple valence state, so they are good candidates for applications in catalysis such as the selective reduction of NOₓ by NH₃,¹⁸ and oxidative dehydrogenation of propane.¹⁹ Moreover, supported vanadium oxides are found to be selective catalysts in a number of catalytic reactions, for example, oxidation of methanol, methane, and olefins, and oxidative conversion of α-xylene to phthalic anhydride.²⁰⁻²² Further research interests will continue in the direction of vanadium-based oxide NCs because of their advantages of...
being cheap and especially because they display high positive redox potential for Li insertion.22–24

As a target for the shape-controlled NC synthesis, recent studies in vanadium oxide NCs have focused on the development of synthetic approaches toward nanotubes, nanobelts, nanofibers, nanowires, nanorods, and so on, as well as their shape-dependent properties. Up to date, some research groups25–27 reported the preparation of size-turnable mixed-valent VO₃ nanostructures via the aging and hydrothermal process of various vanadium sources including bulk V₂O₅ powders, vanadium(V) peroxo gels, and vanadium(V) triisopropoxides using aliphatic amines as structure-directing templates. Furthermore, the distance between the layers in the nanotubes can also be controlled by the alkylic chain length of the structure-directing templates. Zhang et al.28 showed that the belt-, olive-, petal-shaped VO₂ NCs could be synthesized with high concentrations of the reducing agent (specifically oxalic acid) through the hydrothermal route. Baughman et al.15 reported the synthesis of VO₂ nanofibers at room temperature from ammonium metavanadate and acidic ion-exchange resin in water. The resulting VO₂ nanofibers could deliver dramatically higher specific discharge capacities than micrometer-sized VO₂ fibers. Recently, Whittingham’s group has also developed a method to produce vanadium oxide nanofibers with dimensions of less than 140 nm by coating oxides on polylactide fibers.29 Park et al.30 synthesized single-crystalline VO₂ nanowires with rectangular cross sections using a vapor transport method. Schlogl et al.31 presented a reverse micelle technique to prepare V₂O₅ nanorods and nanowires from a micelle technique.32 The aspect ratio (length/width) of the synthesized vanadium oxide nanorods using such a reverse micelle technique was found to be dependent on the water content in the nanotubes. Other metal oxide NCs such as titanium oxide and niobium complexes, and alkyl chain length of capping agents in synthesis mixture. This method can be extended to the synthesis of other metal oxide NCs such as titanium oxide and niobium oxide.

2. Experimental Section

2.1. Starting Materials. All chemicals were used as received without further purification. Vanadium pentoxide (V₂O₅, 99.6%), tetraacetylxyanommonium bromide ([(CH₅)₄NBr or TPA⁺, ≥98%], cetyl trimethylaminommonium bromide ([C₁₆H₃₃N(CH₃)₃]Br or CTA⁻, 95%), tetrapropylammonium bromide ([CH₃(CH₂)₃NBr or TPA⁺, ≥98%], oleylamine (C₁₈H₃₅NH₂ or OM, tech. grade, 90%), hexadecylamine (C₁₆H₃₁NH₂ or HA, tech. grade, 90%), dodecylamine (C₁₂H₂₅NH₂ or DD, ≥98%), and octylamine (C₈H₁₇NH₂ or OC, ≥97%) were purchased from Sigma-Aldrich. Hydrogen peroxide (H₂O₂, 30%) and all solvents used such as toluene and absolute ethanol were of analytical grade and purchased from Reagent ACS.

2.2. Synthesis of Vanadium Oxide Nanocrystals. 2.2.1. Preparation of Complex Precursors: Vanadium(V) Diberoxal Complexes. Preparation of V(V) Diberoxal Complexes (VO(O₂)²⁻(CTA⁺)). A total of 0.14 g (0.77 mmol) of commercial bulk V₂O₅ powders was dissolved in 20 mL of H₂O₂ solution (1.5%) and vigorously stirred at room temperature for 30 min. V₂O₅ powders were completely reacted with dilute H₂O₂ solution to give a homogeneous deep orange V(V) diberoxal aqueous solution (~0.04 mol/L, final pH = 1.5–2.0) with a formula of [VO(O₂)²⁻], according to the procedure reported by Zhang and Yu.34 Then, 40 mL of toluene solution (0.05 mol/L) containing VO(O₂)²⁻ complexes under stirring. The reaction solution was transferred to a 60 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 h. The reaction system was cooled to room temperature using tap water. The vanadium of expensive organometallic compounds. Monodisperse vanadium oxide NCs with different sizes and shapes including nanospheres, nanocubes, nanorices, and nanorods can be achieved by the control of various reaction parameters, such as water content, types of V(V) diberoxal alkylammonium complexes, and alkyl chain length of capping agents in synthesis mixture. This method can be extended to the synthesis of other metal oxide NCs such as titanium oxide and niobium oxide.

Reference:
oxido products were easily precipitated by excess ethanol and dispersed preferably in nonpolar solvents (e.g., toluene, hexane, etc.). The precipitation—redispersion process was repeated several times to purify the producing black OM-capped vanadium oxide nanospheres.

Shape Transformation of Vanadium Oxide Nanospheres into Nanorods by Controlling the Water Content. To investigate the effect of water content on the shape transformation of vanadium oxide nanospheres into nanorods during the solvo-hydrothermal synthesis, a fixed amount of distilled water (water/toluene ratio in volume, W/T = 0:40, 2:40, 8:40, and 20:40) was added to the solution containing VO(O2)2(TOA) complexes. The autoclave was then sealed and heated at 180 °C for 5 h. The NC products recovered in the toluene phase were also washed several times with ethanol to remove the residual oleylamine.

Size-Controlled Synthesis of Vanadium Oxide NCs (Including Nanospheres and Nanoplatelets) from VO(O2)2(CTA) and VO2(O2)2(TPA) Precursors. The above orange complex solids of as-prepared VO(O2)2(TOA) complexes (0.80 g) were completely dissolved in toluene medium (40 mL) under stirring, giving a clear orange solution. To this solution, 0.015 mol (5 mL) of oleylamine was then added. The reaction mixture was transferred to a 60 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 h.

Shape-Controlled Synthesis of Vanadium Oxide NCs by Using Various Capping Aliphatic Amines and Ethanol Used as the Synthesis Medium Instead of Toluene. The obtained orange VO(O2)2(TOA) complex solids (1.1 g) (the above toluene solution containing VO(O2)2(TOA) complexes after toluene evaporation at room temperature) was added to 40 mL of ethanol solution containing other aliphatic amine compounds (0.015 mol) including OM, HA, DD, and OC (depending on the desired particle shape) with stirring for 1 h at 70 °C. The resulting suspension solution was transferred to a 60 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 5 h. The reaction system was then cooled to room temperature, and the black products at the bottom of the vessel were collected. The colloidal alkyl amine capped vanadium oxide NCs were redispersed in toluene and then precipitated by excess ethanol. A similar procedure was employed in the synthesis of other samples as shown in Table 1.

### 2.3. Characterization

The particle sizes and morphologies of the synthesized vanadium oxide NCs were determined at 120 kV by using a JEOL JEM 12300 transmission electron microscope. Samples were prepared by placing a drop of a dilute toluene dispersion of NCs onto a 200 mesh carbon coated copper grid and immediately evaporating at ambient temperature. Scanning electron microscopy (SEM) analyses were carried out to see the overall morphology of the samples on the JEOL 6360 instrument with an accelerating voltage of 3 kV. The average particle dimensions were determined by the size distribution diagrams which were obtained from about 100–150 particles in representative transmission electron microscopy (TEM) pictures of each sample.

The NC products were characterized on a Bruker SMART AXS X-ray diffractometer operated at 120 W power (40 kV, 30 mA) to generate Cu Ka radiation (λ = 1.5418 Å). The X-ray photoelectron spectra (XPS) were taken on a photoelectron spectrometer (KRATOS AXIS-ULTRA) with a monochromatic X-ray source of Al Ka. The operating conditions for recording V 2p, O 1s, and C 1s high-resolution spectra were as follows: 1486.6 eV and 225 W; pass energy of 160 eV with an operating pressure of 10−9 Torr; and acquisition time of 5.75 min. A pressed vanadium oxide pellet under an Ar + bombardment. The V 2p and O 1s signals were measured simultaneously in one energy window. The peaks were deconvoluted by means of standard CasaXPS software (v.2.3.13; product of CasaXPS Software Ltd.) in order to resolve the separate constituents after background subtraction. Fourier transform infrared (FTIR) spectra were measured with a FTS 45 infrared spectrophotometer with the KBr pellet technique. The thermal analyses of the as-made VO2 NCs (∼5 mg) were carried out at a heating rate of 10 °C/min under an air flux up to 650 °C using a Perkin-Elmer TGA thermogravimetric analyzer. Nitrogen adsorption/desorption isotherms were obtained by using a Quantachrome Autosorb-i1 system. Prior to measurements, all samples were degassed at a temperature of 200 °C for at least 2 h. The specific area was calculated from the linear part of the Brunauer—Emmett—Teller (BET) equation (P/Po ≈ 0.05–0.20). The pore size distributions were obtained from the analysis of the desorption branch of the isotherms using the Barret—Joyner—Halenda (BJH) model.

### 3. Results and Discussion

The vanadium oxide NCs were obtained using V(V) diperoxo alkylammonium complexes in the presence of aliphatic amine compounds as capping agents through solvothermal or solvo-hydrothermal treatment at 180 °C for 5 h. Their size and shape were controlled by different reaction parameters: (i) water content in the reaction mixture, (ii) types of V(V) diperoxo alkylammonium complexes (VO(O2)2(TOA), VO(O2)2(CTA), and VO2(O2)2(TPA)), (iii) nature of solvents (toluene and ethanol), and (iv) nature of capping agents (oleylamine (OM), hexadecylamine (HA), dodecylamine (DD), and octylamine (OC)). The effect of these parameters on the size and shape of the final products was systematically examined by TEM measurement. The vanadium oxide NC products obtained under different synthesis conditions are listed in Table 1.

The V(V) diperoxo gels were often obtained via the reaction between V2O5 powders and H2O2 solution.36 Other metal

| Table 1. Synthesis Conditions, Shapes, and Sizes of the As-Made Capped Vanadium Oxide Nanocrystals |
|---|---|---|---|---|---|---|
| Sample | Figure | Precursors [mol] | Surfactants [mol] | Solvents [mL] | T [°C] | t [h] | Shape | Size [nm] |
| 1 | 3a, 4b | VO(O2)2(TOA) | oleylamine | W/T = 0:40 | 180 | 5 | spherical | 4 |
| 2 | 3b | VO(O2)2(TOA) | oleylamine | W/T = 2:40 | 180 | 5 | aggregated spherical | 6–7 |
| 3 | 3c | VO(O2)2(TOA) | oleylamine | W/T = 8:40 | 180 | 5 | short rod | ∼4 × 50 |
| 4 | 3d, e | VO(O2)2(TOA) | oleylamine | W/T = 20:40 | 180 | 5 | aligned rod | 20 × 300 |
| 5 | 3e | VO(O2)2(TOA) | oleylamine | toluene | 180 | 5 | platelet | 10–15 |
| 6 | 4c | VO(O2)2(CTA) | oleylamine | toluene | 180 | 5 | spherical | 5 |
| 7 | 5a | VO(O2)2(TOA) | oleylamine | ethanol | 180 | 5 | cubic | 5 |
| 8 | 5b | VO(O2)2(TOA) | hexadecylamine | ethanol | 180 | 5 | rice | ∼4 × 9 |
| 9 | 5c | VO(O2)2(TOA) | dodecylamine | ethanol | 180 | 5 | thin rod | ∼3 × 50 |
| 10 | 5d | VO(O2)2(TOA) | octylamine | ethanol | 180 | 5 | spherical | 20–25 |

36 Dullberg, P. Z. Z. Phys. Chem. 1903, 45, 129.
peroxo gels were developed for the wet synthesis of transition metal oxides and lamellar structures\textsuperscript{34,37} However, in the case of using V(V) diperoxo gels (e.g., without organic ligands) as precursors, it is hard to control the size and shape of monodisperse NCs due to the heterogeneity in nonpolar media. To overcome this problem, in this study, we used V(V) diperoxo alkylammonium complexes instead of V(V) diperoxo gels.

The V(V) diperoxo tetraoctylammonium complexes, VO(O\textsubscript{2})\textsubscript{2}(TOA), were prepared from the two-phase system of V(V) diperoxo aqueous solution and toluene containing tetraoctylammonium ligands (TOA\textsuperscript{+}) (Scheme 1).

The possible geometry of the [VO(O\textsubscript{2})\textsubscript{2}]\textsuperscript{−} anion is as the peroxide groups parallel each other, perpendicular to the oxo oxygen and with the vanadium atom raised 0.5 Å out of the plane.\textsuperscript{39} Coordination of a TOA\textsuperscript{+} ligand to the vanadium center resulted in the formation of the pentagonal pyramidal oxodiperoxo tetraoctylammonium structure.\textsuperscript{38}

In the second step, the [VO(O\textsubscript{2})\textsubscript{2}]\textsuperscript{−} anions incorporated with the TOA\textsuperscript{+} ligands to yield the V(V) diperoxo tetraoctylammonium complexes VO(O\textsubscript{2})\textsubscript{2}(TOA) through the mass-transfer process of [VO(O\textsubscript{2})\textsubscript{2}]\textsuperscript{−} from the aqueous phase into the toluene phase. It is important to note that the change from a clear in-color to an orange color in the toluene phase, and as seen in eq 1.\textsuperscript{34}

\[
\text{V}_2\text{O}_5 \text{(solid)} + 4\text{H}_2\text{O}_2 \rightarrow 2[\text{VO(O}_2\text{)]_2}\text{\textsuperscript{(gel)}} + 3\text{H}_2\text{O} + 2\text{H}_2\textsuperscript{+} \tag{1}
\]

The possible geometry of the [VO(O\textsubscript{2})\textsubscript{2}]\textsuperscript{−} anion is as the peroxide groups parallel each other, perpendicular to the oxo oxygen and with the vanadium atom raised 0.5 Å out of the plane.\textsuperscript{39} Coordination of a TOA\textsuperscript{+} ligand to the vanadium center resulted in the formation of the pentagonal pyramidal oxodiperoxo tetraoctylammonium structure.\textsuperscript{38}

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\begin{equation}
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\end{equation}

concomitantly from a deep orange in water phase to in-color phase after this step, strongly suggests the presence of [VO(O₂)₂]⁻ anions in the toluene phase (see Scheme 1). The ion pairs of VO(O₂)₂(TOA) complexes formed due to electrostatic interaction (VO(O₂)₂ ⋯ TOA⁺) according to the equilibrium are depicted by eq 2.

\[
[\text{VO(O}_2\text{)}_2]^{-}\text{(water)} + \text{TOA}^+\text{(toluene)} \rightarrow \text{VO(O}_2\text{)}_2(\text{TOA})\text{(toluene)}
\]

(2)

The formation of the VO(O₂)₂(TOA) complexes in the toluene phase is further supported by the FTIR and thermogravimetric analysis (TGA) data. The FTIR spectrum of the VO(O₂)₂(TOA) complex solid (after toluene elimination) exhibits strong absorption FTIR bands characteristic of various vibrationally active groups (Figure 1). The well defined IR bands at 2959, 2918, 2878, and 2852 cm⁻¹ along with the bands at 733 and 720 cm⁻¹ are characteristic of the symmetric and asymmetric methyl and methylene stretches of the TOA⁺ alkyl chains. An IR band is observed at 1455 cm⁻¹ which is attributed to the stretching vibrations of the ammonium cation groups (≡N⁺) of TOA⁺. The IR bands corresponding to stretches of the V(V) diperoxo appear in the 1000–1050 cm⁻¹ region: 960 cm⁻¹ for ν(V=O), 926 cm⁻¹ for ν(O=P–O₆), and 542 cm⁻¹ for ν(V=O). The TGA data for VO(O₂)₂(TOA) complex solid species (Figure 2) reveal a mass loss of 34.8% in the temperature range 120–480 °C, which is attributed to the TOA⁺ decomposition and the combustion of organic groups. Furthermore, the complex species were completely transformed to vanadium oxides as the heating temperature reached 480 °C. A slight increase in mass of approximately 2% between 550 and 650 °C occurred due to the oxidation of reduced vanadium oxides into V₂O₅. These results confirm the formation of VO(O₂)₂(TOA) complexes through the transformation of [VO(O₂)₂]⁻ from aqueous phase into toluene phase in which TOA⁺ cations were coordinated with [VO(O₂)₂]⁻ anions.

Figure 1. FTIR spectrum of the vanadium(V) diperoxo tetractoynammonium complex solid.

Effect of Water Content on the Formation of NCs. Under the solvothermal treatments (e.g., in absence of water in the synthesis solution), at high temperature (180 °C) in organic medium, VO(O₂)₂(TOA) complex precursors are decomposed and generate vanadium monomers and then vanadium nuclei. They are capped by oleylamine molecules. The resulting oleylamine-capped nuclei are hydrophobic and easily dispersed within organic medium, which could grow into nanospheres through an Ostwald ripening process during the solvothermal synthesis. The probable reaction processes for the formation of capping vanadium oxide NCs can be as follows:

![Diagram](Image)

It is important to note that a blue-black color was observed for all as-made vanadium oxide NCs, which corresponds to VO₂, according to the X-ray diffraction (XRD) and XPS results (see below). Figure 3a shows a TEM image of the sample which was synthesized at 180 °C for 5 h without water in the toluene medium (sample 1 in Table 1). It can be clearly seen that the vanadium product consists of uniform quasispherical NCs with a diameter of 4 nm. The selected area electron diffraction (SAED) pattern taken by focusing the electronic beam on a single vanadia particle (inset of Figure 3a and c) composed of bright spots of respective diffraction rings indicated the high crystallinity of vanadium oxide nanospheres.

To verify the role of the TOA⁺ ligands for the formation of NCs, a similar experiment was carried out using V(V) diperoxo compound, [VO(O₂)₂]⁺, as precursor (e.g., without TOA⁺ ligands) instead of VO(O₂)₂(TOA) complexes under the same synthesis conditions. The results showed that no nanospheres were obtained but irregular particles closely aggregated together were formed (S-Figure 1 in the Supporting Information), suggesting the TOA ligands are a key factor for the formation of monodisperse vanadium oxide nanospheres. For the synthesis of vanadium oxide NCs starting from VO(O₂)₂(TOA) complex precursors, the significant effect of water content on the size and shape of vanadium oxide NCs was observed. In this study, the experiments...
were carried out with different amounts of water added in the synthesis solution (Table 1, samples 1–4), while the other synthesis conditions were kept constant. Keeping the toluene volume unchanged (40 mL), the water/toluene ratio (W/T) in volume varied from 0:40 to 2:40, 8:40, and 20:40. It was found that the shape evolution of vanadium oxide NCs is a function of water content. Figure 3 shows representative TEM images of these samples. In the absence of water in the synthesis medium, only uniform quasispherical NCs with an average size of 4 nm were obtained (Figure 3a). While the W/T value was as low as 2:40, aggregated nanoparticles beside some ununiformed small nanorods were formed. Most of the aggregated nanoparticles formed pearl-chain-like structures; however, few isolated nanospheres were still observed (Figure 3b). When the W/T value increased to 8:40, mostly short vanadium oxide nanorods (low aspect ratio) were generated. This indicates that with increasing the water content aggregated particles tend to align and form short rods; however, the rod size distribution is broad with an average diameter of about 6–7 nm and length of 20–30 nm (Figure 3c). It is noted that even when the water content is increased (up to W/T = 8:40), only one phase in the reaction solution is observed. This is ascribed to the water/toluene microemulsion system owing to nanosized water droplets dispersed in a continuous toluene medium and stabilized by surfactant molecules at the W/T interface. The highly dispersed water pools are ideal nanoreactors for producing monodisperse nanoparticles and controlling shapes. However, when the W/T value increased to 20:40, the two water/toluene phases were clearly separated in the synthesis solution. Interestingly, only the nanorod product was formed in the toluene phase (Figure 3d), while no vanadium oxide NCs were essentially observed in the water phase. The vanadium product is composed of uniformly sized and shaped rods with ~20 nm in width and 150–300 nm in length. The high-magnification TEM image clearly demonstrates that the nanorods were quite smooth and straight along their entire length (inset of Figure 3d). Furthermore, the rod diameters were quite uniform. The SAED pattern taken from a single vanadium oxide nanorod in the red square box (Figure 3d inset) reveals the single crystal nature of the nanorod, and it further confirmed that the nanorods' elongation axis was along the [101] direction. It means that the surface energy of the [101] face of the nanoparticles is higher than that of other faces, and the growth by oriented aggregation could be dominant along the preferential direction [101] at the W/T interface, so as to produce nanorods. Water in the synthesis mixture favors generally the formation of nuclei and growth; without or with low water contents in the mixture, the chemical potential of monomer compounds is quite low and their motion is also low, which is disadvantageous for the growth of nanorods. With high water content (e.g., W/T ≥ 20:40), nucleation occurs at high speed, forming a large quantity of tiny crystalline nuclei and consequently leading to low monomer concentration in the bulk solution. Subsequently, the growth rate by oriented aggregation is dominant along the preferential direction (in this work, along the [101] direction).

The increase in nanorod diameter from 7 to 20 nm with the increase of water content to W/T = 20:40 could be explained by a lateral aggregation of individual nanorods along the longitudinal axis and further their fusion to form aligned nanorods at the high water content in the mixture. So far, the syntheses were also carried out at higher W/T ratios (e.g., W/T = 30:40 and 40:40). No obvious change in size and shape (constant aspect ratio) was observed. It implies that high water content (the W/T ratios ≥ 20:40) plays a role to have the two-phase system. In this two-phase system, both nucleation and growth occur at the water/toluene interface. The formed nanorods at the interface can enter the organic phase and could stop growing.

We also believe that the dissolution and growth of vanadium monomers might also result in an overall growth of the nanorods. This suggests that particle size and shape can be controlled by the water content in the reaction mixture under these synthesis conditions. A schematic illustration of the inference from the TEM observation demonstrating the transformation of nanospheres into nanorods is shown in Scheme 2.

In general, nanoporous materials have a large fraction of atoms exposed at surfaces and access to reactant molecules that have attracted intensively for applications to catalysis.
For the surfactant-capped nanoparticles, it is therefore necessary to remove surfactants to generate porosity in the nanomaterial structure. Figure 3e and f represents SEM images of vanadium oxide nanospheres (sample 1) and nanorods (sample 4) after calcination at 550°C for 2 h. As seen in Figure 3e for the vanadium oxide nanosphere sample, the SEM image reveals that the spherical morphology with some interlinked 3-D microspheres aggregated into bigger ones was observed and inside each microsphere is mainly composed of monodisperse 4 nm sized nanospheres. However, the SEM result of the calcined nanorod sample (Figure 3f) shows that the product consists of individual nanorods with ∼20 nm in diameter and 150–300 nm in length, which is comparable with those observed in the high-magnification image (S-Figure 2 in the Supporting Information). As seen in S-Figure 2 (Supporting Information), each nanorod is quite smooth and straight along the entire length.

Figure 4 shows the wide-angle XRD patterns of the as-made vanadium oxide nanosphere (sample 1 in Table 1) and nanorod (sample 4) samples before and after calcination at 550 °C for 2 h. The X-ray pattern (Figure 4a) of the as-made samples 1 and 4 corresponds to monoclinic rutile-type VO₂ (JCPDS card no. 44-0253, \(a = 0.4554\) nm, \(c = 0.2856\) nm).\(^{50,51}\) However, after calcination, the XRD patterns of the samples 1 and 4 exhibit the orthorhombic V₂O₅₋ₓ phase (space group \(Pmmn\), \(a = 11.516\) Å, \(b = 3.566\) Å, \(c = 3.777\) Å; JCPDS card no. 41-1426).\(^{52}\) Furthermore, their color changed from blue-black to yellow after calcination (see Figure 6d). This indicates the transformation from the monoclinic rutile phase to the orthorhombic phase of these samples (Figure 4b,c). No other phases were detected in the XRD patterns, suggesting the pure orthorhombic structure of the V₂O₅₋ₓ NCs. The particle size of the calcined vanadium oxide nanosphere sample calculated from the (001) reflections using the Debye–Scherer equation is 5.2 nm,\(^{53}\) which is in agreement with the sizes determined from the above TEM (Figures 3a and 5b). It is important to note that the relative intensity of the (101) diffraction peak of the nanorods is much higher than that of the nanospheres, which indicates their anisotropic structure and is in agreement with TEM and SAED results (Figure 3d).

To study the influence of the alkyl chain length of vanadium complex ligands on the formation of vanadium oxide NCs, three different types of V(V) diperoxo alkylammonium complexes with different alkyl chain ligands including VO(\(O_2\))(TOA), VO(\(O_2\))(CTA), and VO(\(O_2\))(TPA) (see details...
Metal complex precursors with longer alkyl chain and shape of the resulting NCs can be affected by steric activity of monomer complexes and, consequently, the size of samples also composed of bright diffraction spots indicated patterns (inset of Figure 6a). All of the syntheses were carried out under the same conditions as those for sample 1 in Table 1. (d) Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.

The effect of steric ligands of vanadium complexes on the size of vanadium oxide NCs, TEM images and corresponding SAED patterns of the VO2 NC samples prepared from different vanadium complex precursors (e.g., various ligands): (a) VO(O2)2(TPA), (b) VO(O2)2(CTA), and (c) VO(O2)2(TOA). All of the syntheses were carried out under the same conditions as those for sample 1 in Table 1. (d) Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.

Photograph of multigrams of the as-made blue-black VO2 nano-}

shape of the resulting NCs can be affected by steric activity of monomer complexes and, consequently, the size of samples also composed of bright diffraction spots indicated patterns (inset of Figure 6a). (d) Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.

In the Experimental Section) were used as starting precursors. The alkyl chain length in the order TOA > CTA > TPA. The syntheses were conducted under the same conditions (samples 5 and 6, Table 1). According to their XRD patterns, all the calcined products obtained from these different complex precursors have the orthorhombic phase of V2O5. (Figures 4 and 5). The particle sizes of calcined samples 5 and 6 calculated from the (001) reflections are ~12.0 and ~6.5 nm, respectively. Representative TEM images of these as-made NC products are also presented in Figure 6. The vanadium oxide sample prepared from VO(O2)2(TPA) is composed of irregular nanoplatelets with diameters of ~10–15 nm (Figure 6a). However, using VO(O2)2(CTA) and VO(O2)2(TOA), the quasispherical NCs were obtained with average diameters of ~4 and ~5 nm, respectively (Figure 6b and c), in agreement with the particle sizes obtained by XRD spectra. The corresponding SAED patterns (inset of Figure 6a–c) of these vanadium oxide samples also composed of bright diffraction spots indicated the high crystallinity of vanadium oxide NCs. In general, the activity of monomer complexes and, consequently, the size and shape of the resulting NCs can be affected by steric ligands.34 Metal complex precursors with longer alkyl chain ligands diffuse slower through the growth solution, and they are also decomposed more slowly.35 In the case of TPA as complex ligands, their alkyl chain is shortest, the complex activity was very high (rapid diffusion and decomposition), many nuclei were formed at the nucleation stage and aggregated immediately at the growth stage, and as a result a larger particle size was obtained. However, longer alkyl chain ligands such as TOA and CTA can balance the nucleation and growth rates, producing smaller NCs. Based on the TEM results, vanadium complexes with the longer alkyl chains (TOA and CTA), as compared to that of TPA, were decomposed more slowly to generate smaller nanoparticles. Therefore, it can be suggested that the particle sizes gradually increased from ~4 to ~5 and 10–15 nm due to the decrease of alkyl chain length of complex ligands from TOA to CTA and then TPA.

It is important to note that, using this process, multigram-scale vanadium oxide NCs can be achieved in a single batch. For example, using VO(O2)2(CTA) complexes as precursors, about 6.8 g of oleylamine-capped quasispherical vanadium oxide NCs was obtained in a single run (Figure 6d). The blue-black color of the products suggests that V5+ ions had been reduced to V4+ by decomposing the precursors during synthesis,44 which is further confirmed by the XPS results (see below).

To understand the role of solvent medium on the particle size and shape of the resulting vanadium oxide NCs during the synthesis,56 the experiment was carried out using VO(O2)2(TOA) complexes, and ethanol instead of toluene as reaction medium, while the other parameters were kept constant. Uniform vanadium oxide nanocubes with sizes of ~5 nm in diameter were obtained (Figure 7a). This indicates the change in size and shape of vanadium oxide NCs from ~4 nm sized nanospheres (see Figure 3a) to ~5 nm sized nanocubes when toluene was substituted by ethanol as medium in the reaction system. However, the product yield remained unchanged. This phenomenon may be due to the different dielectric constant and polarity of ethanol and toluene. The effect of different solvent media on the size and shape of NCs will be systematically studied and reported in a following paper.57,58

Furthermore, to gain further insights into the steric effect of the capping ligands on the size and shape of vanadium oxide NCs, different alkyl chain lengths of the capping aliphatic amines were used, such as oleylamine (OM, C18),

Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.

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Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.

Photograph of multigrams of the as-made blue-black VO2 nanosphere solids (6.8 g) and the calcined yellow V2O5 nanosphere solids (5.7 g) obtained in a single batch.
hexadecylamine (HD, C\textsubscript{16}), dodecylamine (DD, C\textsubscript{12}), and octylamine (OC, C\textsubscript{8}). The syntheses were carried out in ethanol as reaction medium, and VO\textsubscript{2}(TOA) complexes were used as vanadium precursors (Figure 7 and Table 1). The mass of VO\textsubscript{2}(TOA) complex solid (1.1 g) and volume of ethanol (20 mL) were kept the same in all syntheses (see details in the Experimental Section). It is found that the vanadium oxide NCs exhibit various shapes, including cubic, ricelike particle, rod, and spherical particles, when the alkyl chain length of aliphatic amines is altered (Figure 7). In general, the effect of the capping alkyl chain length is noticeable, as (i) it defines the lateral spacing between the particles and (ii) it is responsible for their anisotropic growth into various shapes such as ricelike and rod. Primary NCs capped by shorter alkyl chain ligands are more mobile and more reactive than those by longer ones, because they are less sterically impeded, which leads to faster diffusion and faster nucleation–growth kinetics\cite{(59) Lee, S. H.; Kim, Y. J.; Park, J. Chem. Mater. 2007, 19, 4670–4675. (60) Scher, E. C.; Manna, L.; Alivisatos, A. P. Philos. Trans. R. Soc. London, Ser. A 2003, 361, 241–257. (61) Zhao, N.; Pan, D.; Nie, W.; Ji, X. J. Am. Chem. Soc. 2006, 128, 10118–10124.}, and anisotropic growth is favored\cite{(59) Lee, S. H.; Kim, Y. J.; Park, J. Chem. Mater. 2007, 19, 4670–4675. (60) Scher, E. C.; Manna, L.; Alivisatos, A. P. Philos. Trans. R. Soc. London, Ser. A 2003, 361, 241–257. (61) Zhao, N.; Pan, D.; Nie, W.; Ji, X. J. Am. Chem. Soc. 2006, 128, 10118–10124.}.

Our results revealed that when the long alkyl chain OM (C\textsubscript{18}) was used, uniform vanadium oxide nanocubes with sizes of 5 nm in diameter were produced (Figure 7a). However, when HD (C\textsubscript{16}) was used instead of OM, elongated particles with a ricelike shape and a size of about 4 nm × 9 nm were formed (Figure 7b). Furthermore, when HD was substituted by DD (C\textsubscript{12}), the formation of thin nanorods with an average size of 3 nm × 50 nm was observed (Figure 7c). This suggests that shorter alkyl chain ligands favor an anisotropic growth resulting in the formation of nanorods. However, with very short alkyl chain ligands (< C\textsubscript{12}) (in this work, we used OC (C\textsubscript{3})), only spherical particles with a broad particle size distribution and large diameter of 20–25 nm were observed (Figure 7d). The dispersity of the NCs prepared from HD, DD, and OC (shorter alkyl chain lengths compared to that of OM) was not as good as that of the NCs from OM, which could be due the smaller sterical barrier\cite{(59) Lee, S. H.; Kim, Y. J.; Park, J. Chem. Mater. 2007, 19, 4670–4675. (60) Scher, E. C.; Manna, L.; Alivisatos, A. P. Philos. Trans. R. Soc. London, Ser. A 2003, 361, 241–257. (61) Zhao, N.; Pan, D.; Nie, W.; Ji, X. J. Am. Chem. Soc. 2006, 128, 10118–10124.}.

The corresponding SAED patterns (inset of Figure 7) of cubic, ricelike, and spherical vanadium oxide particles exhibit a set of sharp diffraction spots which are characteristic of single crystalline of monoclinic rutile-type VO\textsubscript{2} structure.

Furthermore, as seen in the insets of Figures 3d and 7c, for samples 4 and 9, the SAED patterns of these samples are quite similar, indicating a good lattice matching between the two different samples. The same set of spots of sample 9 compared to that of sample 4 suggests the thin rods also elongated along the [101] direction, which is consistent with their XRD results.

It is believed that the short alkyl chain length of aliphatic amines (< C\textsubscript{12}) as capping ligands could be hard to control the nucleation and growth because of much fast diffusion and growth kinetics. This can be concluded that the shape evolution of NCs can also depend on the alkyl chain length of the capping agents.

X-ray photoelectron spectroscopy (XPS) is a surface-specific technique that was also used to study the oxidation states and the surface composition of the as-made and calcined vanadium oxide nanosphere samples (sample 1 before and after calcination). The survey XPS spectra of these samples in a wide energy range are shown in Figure 8. Besides carbons and nitrogens, no impurities were found. However, the intense C 1s and N 1s peaks of the as-made samples as compared to those of the calcined sample can be assigned to the oleylamine ligand capped on the NC surface. The positions of the XPS peaks were corrected using the C 1s core level taken at 285 eV as the binding energy (BE) reference. The XPS spectra of V 2p together with O 1s are presented in Figure 9. The deconvolution data of the spectra are summarized in Table 2\cite{(62) Olivetti, E. A.; Kim, J. H.; Sadoway, D. R.; Asatekin, A.; Mayes, A. M. Chem. Mater. 2006, 18, 2828–2833. (63) Barbero, B. P.; Cadus, L. E.; Hilaire, L. Appl. Catal., A 2003, 246, 237–242. (64) Guimarães, J. L.; Abbate, M.; Betim, S. B.; Alves, M. C. M. J. Alloys Compd. 2003, 352, 16–20.}. Both the as-made and calcined vanadium oxide nanosphere samples show the V 2p states composed of two components originating from the spin–orbit splitting of V 2p\textsubscript{3/2} and V 2p\textsubscript{1/2}, which are restricted to a ratio of 1.8:1.0 and the separation energy Δ = 8.5 eV. The V 2p\textsubscript{3/2} peak has a small full width, 2.5–3.0 eV, at half-maximum (fwhm), and the V 2p\textsubscript{1/2} peak has a larger fwhm, 5.0–5.5 eV, due to multiplet effects.\cite{(62) Olivetti, E. A.; Kim, J. H.; Sadoway, D. R.; Asatekin, A.; Mayes, A. M. Chem. Mater. 2006, 18, 2828–2833. (63) Barbero, B. P.; Cadus, L. E.; Hilaire, L. Appl. Catal., A 2003, 246, 237–242. (64) Guimarães, J. L.; Abbate, M.; Betim, S. B.; Alves, M. C. M. J. Alloys Compd. 2003, 352, 16–20.} For the as-made sample 1, V 2p\textsubscript{3/2} and V 2p\textsubscript{1/2} peaks at 516.2 and

![Figure 8](image81x591 to 261x752)

**Figure 8.** Survey XPS spectra of as-made vanadium oxide nanospheres (a) before and (b) after calcination in air at 550 °C for 2 h (sample 1 in Table 1).

![Figure 9](image346x55), 16–20.

**Figure 9.** XPS spectra of V 2p and O 1s peaks and their deconvolution of the as-made vanadium oxide nanosphere sample (a) before and (b) after calcination at 550 °C for 2 h.
Table 2. XPS Binding Energies of O 2s, V 3p, V 3s, V 2p, and O 1s Peaks in the As-Made Vanadium Oxide Nanosphere Sample before and after Calcination at 550 °C for 2 h (Sample 1 in Table 1)

<table>
<thead>
<tr>
<th>Sample</th>
<th>O 2s</th>
<th>V 3p</th>
<th>V 3s</th>
<th>V 2p</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-made</td>
<td>524.1</td>
<td>521.2</td>
<td>516.2</td>
<td>524.1</td>
<td>520.7</td>
</tr>
<tr>
<td>calcined</td>
<td>524.1</td>
<td>521.2</td>
<td>516.2</td>
<td>524.1</td>
<td>530.7</td>
</tr>
</tbody>
</table>

*BE = 0.1 eV.

Figure 10. TGA/DTA curves of (a) the as-made OM-capped vanadium oxide nanospheres and (b) the as-made OM-capped VO2 nanorods (samples 1 and 4 in Table 1).

Figure 11. FTIR spectrum of the as-made OM-capped vanadium oxide nanospheres (sample 1 in Table 1).

524.1 eV, respectively, which are attributed to $V^{4+}$ were observed. Non-XPS peaks corresponding to $V^{5+}$ were detected (Figure 9a), suggesting that the surface chemical composition in the as-made NC sample is VO$_2$. However, the calcined sample 1 exhibits the presence of both $V^{4+}/V^{5+}$ oxidation states (Figure 9b). Both V 2p$_{3/2}$ and V 2p$_{1/2}$ peaks at 517.2 and 525.5 eV, respectively, which are characteristic of vanadium in the +5 oxidation state, are present. Simultaneously, the V 2p$_{3/2}$ and V 2p$_{1/2}$ peaks at 516.2 and 524.1 eV, respectively, corresponding to the $V^{4+}$ oxidation state were observed. From the relative areas of the $V^{4+}$ and $V^{5+}$ contributions, the surface vanadium was found to be $\sim 65\%$ $V^{5+}$ and $\sim 35\%$ $V^{4+}$ for the calcined nanosphere sample (see Table 2). It can be concluded that the change of color from blue-black to yellow upon calcination in air could be due to the transformation from the $V^{4+}$ to $V^{5+}$ oxidation state (see Figure 6d).

Oxygen bonded to vanadium atoms in the as-made vanadium oxide NC sample (sample 1) exhibits an O 1s peak (Figure 9a) related to O–V (530.7 eV). However, the O 1s peak of this sample after calcination shows it is composed of two components. The deconvolution peak at 530.4 eV was assigned to the O=V groups, and another peak at a higher binding energy of 531.0 eV was attributed to the O–V ones, which are related to the oxygen in the crystal lattice of vanadium oxides. Based on the corresponding areas of the vanadium and oxygen XPS peaks obtained by deconvolution, the molar ratio of V/O determined from the surface chemical composition of the as-made and calcined sample 1 was, respectively, (1.0):(2.0) and (1.0):(2.3). Thus, the chemical formula is, respectively, VO$_2$ and V$_2$O$_4$.

Figure 10 shows thermogravimetric differential thermal analysis (TGA-DTA) curves of the OM-capped VO$_2$ nanosphere and OM-capped VO$_2$ nanorod samples (samples 1 and 4 in Table 1). For the nanosphere sample (Figure 11a), the steep weight loss (22%) appeared around 100–390 °C. However, the corresponding DTA curve shows two exothermic peaks at 215 and 324 °C, which are related to the decomposition and combustion of capping agents on the particle surfaces during heating. A gradual mass gain of VO$_2$ (∼2%) above 411 °C accompanied by a sharp endothermic peak at 593 °C could be related to oxidation of the vanadium dioxide framework from $V^{4+}$ to $V^{5+}$, as reported by Brandstatter and Riedmann. The total mass loss of nanorods was 28%, quite similar to that of the nanospheres, 22% (samples 1 and 2). However, for the VO$_2$ nanorod sample (Figure 11b), the presence of an additional broad exothermic peak at a higher temperature at 431 °C could be due to strongly held surfactant molecules blocked between nanorods, in good agreement with our previously published results.

The FTIR spectrum of the as-made oleylamine (OM)-capped vanadium oxide nanosphere sample (e.g., sample 1 in Table 1) is shown in Figure 11. The FTIR bands at 2925 and 1625 cm$^{-1}$ are assigned to the C–H and C=C stretching modes of alkyl chains in oleylamine, respectively. The band at 1458 cm$^{-1}$ could be attributed to the N=H bending and N=C stretching modes of O=NH$_2$ groups in oleylamine capping on vanadium dioxides. Furthermore, the IR bands at 620 and 927 cm$^{-1}$ corresponding to the vibrations of V=O–V and O=(V)$_3$, respectively, along with an intense FTIR band at 1022 cm$^{-1}$ attributed to the V=O vibration are characteristic of vanadium oxides. The presence of these FTIR bands suggests that oleylamine molecules are protonated.
bound to the surface of VO$_2$ NCs. Similar results for the other aliphatic amine capped vanadium oxide NC samples were also observed (not shown).

The BET specific surface areas and pore size distributions of the various samples after calcination were obtained by nitrogen adsorption/desorption isotherms and are summarized in Table 3 and S-Figure 3 in the Supporting Information. For the calcined nanosphere samples (samples 1 and 2 in Table 1), the BET surface area was 70.5 and 68.5 m$^2$/g for sample 1 and sample 2, respectively. The BET surface area of sample 1 is higher than that of sample 2 due to its smaller particle sizes. The average pore diameter with narrow mesopore size is around 16.5 and 19.5 nm for sample 1 and sample 2, respectively.

For samples 3 and 4 (Table 1) after calcination, the BET surface area values are 42.0 and 32.0 m$^2$/g with an average pore size of 37.0 and 51.0 nm, respectively. The pore diameter of sample 4 is somewhat larger than that of sample 3 due to the length difference of the rods. It is also noted that average pore diameters of the nanosphere samples (samples 1 and 2) are smaller than those of the nanorod samples (samples 3 and 4) due to the compact structure. The high specific surface areas of these nanoparticle samples after calcination can be explained by the particle surfaces being protected by the capping agent and the nanoparticle surface being preserved during thermal procedures. The properties of such NCs could make them an interesting system for future studies in catalysis.

<table>
<thead>
<tr>
<th>sample</th>
<th>size and shape [nm]</th>
<th>$S_{\text{BET}}$ [m$^2$/g]</th>
<th>$V_{\text{BH}}$ [cm$^3$/g]</th>
<th>avg pore diameter [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4 nm spheres</td>
<td>70.5</td>
<td>0.100</td>
<td>16.5</td>
</tr>
<tr>
<td>2</td>
<td>6–7 nm aggregated spheres</td>
<td>68.5</td>
<td>0.160</td>
<td>19.5</td>
</tr>
<tr>
<td>3</td>
<td>~9 × 50 nm rods</td>
<td>42.0</td>
<td>0.210</td>
<td>37.0</td>
</tr>
</tbody>
</table>

4. Conclusion

We have developed a new solvo-hydrothermal route to synthesize monodisperse vanadium oxide NCs from vanadium(V) diperoxotetraalkylammonium complexes in aliphatic amine/toluene or aliphatic amine/toluene/water. Commercial bulk V$_2$O$_5$ powders were used as a starting vanadium source. This approach is simple, economical, and easily scaled up for products. The transformation of vanadium oxide nanospheres into short nanorods as well as aligned nanorods can be controlled by water content in the synthesis mixture. Furthermore, the shape evolution of vanadium oxide products from nanospheres to nanoplatelets, nanocubes, and then to nanorods was also controlled by the steric ligands of vanadium complexes as well as the alkyl chain length of capping aliphatic amine agents in ethanol medium.

The obtained vanadium oxide NC products before calcination are monoclinic rutile VO$_2$ structure with black color, which is however converted to the orthorhombic V$_2$O$_4$-$\delta$ structure with yellow color upon the calcination procedure. The XPS results of these samples revealed that only V$^{4+}$ was observed before calcination, while the coexistence of two vanadium oxidation states (V$^{4+}$ and V$^{5+}$) and two components of oxygen corresponding to O=V and O–V groups on the vanadium pentaoxide NC surface was identified. The surface chemical composition of the vanadium oxide NC sample is VO$_2$ and V$_2$O$_{2-x}$ (x = 0.4) before and after calcination, respectively. The high surface area of the vanadium oxide NC samples after calcination could be beneficial for potential applications in many fields of advanced nanotechnology, particularly in catalysis and chemical biological sensors. Furthermore, the synthetic method developed here can be extended to the synthesis of other nanocrystalline oxides and is potentially useful for large-scale production of nanomaterials.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a strategic grant. The authors would like to thank Prof. S. Kaliaguine for stimulating discussions and comments.

Supporting Information Available: TEM image of OM-capped VO$_2$ NCs; high-magnification TEM image of calcined vanadium oxide nanorods; nitrogen adsorption/desorption isotherms and BJH pore size distributions of vanadium oxide nanocrystal samples. This material is available free of charge via the Internet at http://pubs.acs.org.
Solvo-hydrothermal Approach for the Shape-Selective Synthesis of Vanadium Oxide Nanocrystals and Their Characterization

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SUPPORTING INFORMATION

S-Figure 1. TEM image of OM-capped VO₂ NCs synthesized from the solvothermal reaction of vanadium(V) diperoxo (without TOA⁺ ligands) in oleylamine/toluene at 180 °C for 5 h.
S-Figure 2. High-magnification TEM image of the calcined vanadium oxide nanorods (calcined sample 4 in Table 1).
**S-Figure 3.** (a) Nitrogen adsorption (filled symbols) and desorption (open symbols) isotherms and (b) BJH pore size distributions of vanadium oxide nanocrystal samples after calcination at 550 °C for 2 h (samples 1-4 in Table 1).