Oxygen storage in transition metal-doped bixbyite vanadium sesquioxide nanocrystals

Lauren C. Reimnitz¹, Thiri Lwin¹, Mario Lopez¹,², Delia J. Milliron¹*

1 – McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, United States
² – Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States; current affiliation: Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States

*email: milliron@che.utexas.edu

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Abstract

Bixbyite vanadium sesquioxide (V₂O₃) is a metastable polymorph of vanadium oxide that has been shown to have a significant oxygen storage capacity with very low temperature oxidation onset. In this work, bixbyite V₂O₃ nanocrystals were synthesized with titanium and manganese dopants.
Doped materials with varied dopant concentration were synthesized, and all were incorporated as aliovalent metal ions. The oxygen storage capacity of these nanocrystal materials was evaluated over ten oxidation and reduction cycles. It was found that over these ten cycles, the oxygen storage capacity of all the materials fell drastically. In situ X-ray diffraction evidence shows that manganese-doped materials degrade into an amorphous manganese-containing vanadate, while titanium-doped materials form crystalline degradation products. In all cases, this degradation causes an increase in the minimum mass achieved during oxygen release, indicating irreversible oxidation.

**Introduction**

The bixbyite phase of vanadium sesquioxide (V$_2$O$_3$), a metastable phase of the material, was first reported in 2011 by Weber et. al.\(^1\) In 2015, a method to synthesize the pure bixbyite phase V$_2$O$_3$ as colloidal nanocrystals was described by Bergerud et al..\(^2\) Shortly after, it was discovered that this material exhibits excellent reversible oxygen storage capacity, with a remarkably low oxidation onset temperature, owing to its intrinsic oxygen vacancies.\(^3\) This property has motivated investigation into ways to maximize the oxygen storage capacity and thermal and environmental stability of this material, to facilitate its potential application as an oxygen storage material (OSM) in automotive catalysts, where it could address problems with cold start.

Automotive catalysis has been discussing the cold start problem for quite some time. Catalytic converters were introduced in the United States by General Motors in 1975, consisting of alumina support with small amounts of platinum and palladium catalyst material.\(^4\) Their use was made nearly ubiquitous by emissions standards introduced by the US Environmental Protection Agency in that year, and practically required by updated standards as an amendment to this legislation in 1990.\(^5\) Modern catalytic converters have added cerium oxide, or ceria, to the catalyst bed to
promote high conversion and efficiency at low air-to-fuel ratios in the exhaust stream. Ceria, while it has enjoyed decades of use as the OSM of choice in the automotive industry, is not without shortcomings. Below about 300°C, the ceria surface is not reactive with oxygen. An inactive OSM is one reason that automotive catalysts are virtually inactive until the converter reaches an operation temperature of at least 300°C. Thus high levels of emission are observed during the first few minutes of operation of an automotive engine, and this is referred to by the catalysis community as the “cold start” problem. By contrast, V₂O₃ nanocrystals have been shown to absorb oxygen from an atmosphere at temperatures as low as 100°C and have a very similar oxygen storage capacity (OSC) to this industry standard material. It struggles, however, with poor stability upon cycling, owing to the wide variety of structures available to the large number of vanadium oxides that can be formed, reflected in the complexity of its phase diagram.

Doping is a commonly employed strategy in materials design for applications where stability is desired. In fact, OSMs for automotive catalysts have long used dopants to optimize performance. Since at least the 1990s, the ceria OSMs in most auto catalytic converters have included these deliberate impurities, which increase the material’s useful lifetime and its OSC. Through experimental and computational methods, it has been shown that zirconium impurities, as Zr⁴⁺, introduce strain to the ceria lattice that prevents sintering, which causes a decrease in capacity over the material’s lifetime, while increasing OSC by causing partial reduction of cerium ions. Studies on divalent dopants in ceria show that the interplay between charge imbalance and lattice strain has strong impacts on oxygen storage capacity. In this work, doped V₂O₃ nanocrystals are synthesized to investigate the impact of dopants on the OSC and cycling stability of this novel OSM. Titanium and manganese dopants were chosen, as transition metals on either side of vanadium on the periodic table. Incidentally, titanium dopants have been studied before in
vanadium oxides, where titanium was shown to stabilize the corundum paramagnetic phase.\textsuperscript{18} It has also been shown to increase the monoclinic-to-rutile transition temperature in VO\textsubscript{2}.\textsuperscript{19,20} Likewise, manganese is one of many dopants that have been studied as incorporated into the layered material V\textsubscript{2}O\textsubscript{5} for use in battery and energy storage applications.\textsuperscript{21–27}

**Results and Discussion**

V\textsubscript{2}O\textsubscript{3} particles were prepared with varied concentrations of titanium and manganese dopants. Changes in the oxidation state of the metal ions caused by doping were evaluated by X-ray photoemission spectroscopy (XPS). The OSC for each sample was measured by thermogravimetric analysis (TGA). The crystallinity and crystal phase for each material was evaluated by ex-situ X-ray diffraction (XRD) before and after processing in TGA. Further, the crystal structure of the materials during oxidation and reduction were followed by in situ XRD, which revealed different degradation mechanisms for materials with different compositions.

![Figure 1](image)

**Figure 1.** Transmission electron micrographs of a) undoped, b) 10\% Ti-doped, and c) 10\% Mn-doped V\textsubscript{2}O\textsubscript{3} nanocrystals. Mn dopants cause a change in shape to bipyramidal. Scale bars are 50 nm.

Titanium doping resulted in particles of size and shape very similar to undoped particles. Both types of nanocrystals have flower morphology and diameter of 20-40 nm, accompanied by some smaller side products, possibly the result of secondary nucleation during synthesis. Molybdenum
doping resulted in highly faceted particles with a wide distribution of sizes, ranging from 3 to 20 nm across the longest dimension. Very small, round particles observed here may be from secondary nucleation as well, which can create small crystals that do not have the opportunity to grow. The larger particles are bipyramidal in shape, with rhombohedral projections between 5 and 20 nm across the dark middle, and between 10 and 25 nm across from tip to tip.

![Image](image_url)

**Figure 2.** X-ray photoemission spectra (XPS) of the doped V$_2$O$_3$ nanocrystals. (a) Mn 2p spectra and (b) O1s and V2p spectra collected for Mn:V$_2$O$_3$ nanocrystals. (c) Ti 2p and (d) O1s and V2p spectra collected for Ti:V$_2$O$_3$ nanocrystals. The O1s and V2p region for undoped V$_2$O$_3$ nanocrystals is shown in both panels b and d for reference.

XPS of the doped vanadium oxides (Figure 2) show the 2p transitions for vanadium in all the samples, along with the 2p transitions for the dopant elements. Survey spectra are shown in Figure S2. Ti- and Mn-doped samples all show a slight shift of the V 2p transitions to higher binding
energy. The oxidation state of the dopant atoms can be determined by analysis of their 2p transitions. The Mn 2p spectrum shows a shake-up feature at 647 eV, diagnostic of the Mn$^{2+}$ state.\textsuperscript{28} To further support this finding, the Mn 3s spectrum was collected (high resolution spectra and fits shown in Figure S4). The 3s spectrum has two peaks, due to correlation with the unfilled 3d$^5$ shell. The binding energy difference between the 3s $^7$S and $^5$S multiplet component peaks was found to be 6.5 eV for both the 5\% and 10\% doped samples, consistent with previous literature observing Mn in the 2+ oxidation state.\textsuperscript{29} The titanium 2p peaks have a spin-orbital splitting of 5.7 eV each, which is consistent with reports for TiO$_2$, where Ti is in the 4+ oxidation state.\textsuperscript{30} Both of these ions are larger than the native V$^{3+}$ ion, at 0.74 and 0.83 nm for Ti$^{4+}$ and Mn$^{2+}$ with 6-fold coordination, respectively, compared to 0.64 nm for V$^{3+}$, so they are expected to have similar effect on lattice strain.\textsuperscript{31} While both dopants are larger than the host ion, they introduce charge imbalance in opposite directions.

![Figure 3. Bixbyite M:V$_2$O$_3$ nanocrystals with varied dopant composition were measured for ten complete oxidation and reduction cycles. The mass during the entire measurement was normalized.](image-url)
to the weight measured at the end of the first complete cycle’s reduction step, where the fractional mass gained is set to 0. Reduction was conducted at 300°C under flow of nitrogen, while oxidation was conducted at 150°C under flow of air.

A representative group of the thermogravimetry curves for a ten-cycle experiment is shown in Figure 3. In this experimental procedure, each sample was subjected to ten oxidation and reduction cycles. Each cycle consists of a reduction step at 300°C in nitrogen, and an oxidation step at 150°C in air. This temperature program is represented by the grey dashed line. The colored curves correspond to the mass fraction of the sample, where mass fraction of zero is defined as the mass after the first oxidation and reduction steps, to account for differences in oxidation from air exposure, water content, and ligand content. This measure allows for the calculation of an oxygen storage capacity (OSC) for each cycle number, which can be represented as the difference in mass fraction at the minimum weight during reduction and the maximum weight during oxidation.
Figure 4. Oxygen storage capacity of Mn- and Ti-doped nanocrystals (a and b, respectively) over ten oxidation and reduction cycles. The maximum fractional mass occurring after each oxidation step for Mn- (c) and Ti-doped (d) nanocrystals. The minimum fractional mass after each reduction step for Mn- (e) and Ti-doped (f) nanocrystals.

All the doped samples had higher OSC than undoped nanocrystals for their first six cycles of oxidation and reduction. However, for all samples, the OSC dropped dramatically during ten cycles. The Ti-doped samples both maintained higher OSC during all ten cycles, ending with an
OSC 20-30% higher than that of undoped V$_2$O$_3$. Vanadium oxide doped by Mn had lower OSC than undoped nanocrystals after 10 cycles. The OSC is determined by the difference between the maximum weight and the minimum weight during each oxidation and reduction cycle (Figure 4 a-b), and tracking those maximum and minimum values provides more information about the decrease in OSC with cycle number (Figure 4 c-f). It is immediately evident that the minimum mass fraction for all samples rose sharply in the first four cycles, indicating irreversible oxidation and suggesting a kinetic barrier to oxygen release during the reduction half-cycle. There is a correlated drop in maximum mass fraction after oxidation for Mn-doped nanocrystals. However, for the Ti-doped samples, the maximum and minimum fractional masses both drop nearly linearly with cycle number after cycle 5, suggesting that the Ti-doped samples are degraded by some separate or additional mechanism.

The as-synthesized nanocrystals and the products after the ten oxidation and reduction treatment as described above were analyzed by powder X-ray diffraction. The results are shown in Figure 5. Reference XRD patterns are shown for bixbyite V$_2$O$_3$ in black, the thermodynamically preferred corundum phase of V$_2$O$_3$ in red, rutile VO$_2$ in green, and rutile TiO$_2$ in turquoise, all at the bottom. The samples show good crystallinity before TGA cycling and exist in the bixbyite crystal structure, apart from highly Mn-doped V$_2$O$_3$, which shows only very broad diffraction signal. Two peaks in the pattern for 10% Ti:V$_2$O$_3$, at 2θ of 28.6° and 47.5° (marked with a star in Figure 5), were not indexed to a known phase of titanium or vanadium oxide. For samples doped up to 5%, only bixbyite V$_2$O$_3$ peaks are observed. After ten cycles of oxidation and reduction, the crystallinity in both the Mn-doped samples has all but disappeared, indicating degradation to form some non-crystalline product. The undoped and Ti-doped samples lose intensity from the original bixbyite phase and develop new peaks due to crystalline impurities. The major impurities are from the
thermodynamically preferred corundum structure of $V_2O_3$ and rutile $VO_2$. While diffraction peaks of rutile $TiO_2$ could not be differentiated from those of $VO_2$, the amount of titanium incorporated into the material is quite small, so we expect that these peaks appear due to the formation of rutile $VO_2$.

Figure 5. *Ex situ* X-ray diffraction of all dopant levels (a) before and (b) after ten oxidation and reduction cycles in TGA. Calculated reference patterns are shown for the as-synthesized bixbyite $V_2O_3$ phase, the native corundum $V_2O_3$, and rutile $VO_2$, which may have some contribution to patterns for the samples after cycling.
Figure 6. In-situ X-ray diffraction of a) Mn-doped and b) Ti-doped V₂O₃ nanocrystals during the oxidation half-cycle at 150°C in air. The diffraction pattern is truncated to show q between 3 and 4.5 Å⁻¹, highlighting changes to the (440) and (622) peaks. The 1D patterns at 10 minutes (red) and 50 minutes (green) are reproduced above the in-situ scans for clarity.

To investigate the different mechanisms of oxidation and reduction for doped V₂O₃, in situ X-ray diffraction was conducted. In Figure 6, the oxidation half-cycle is shown in reciprocal space for q between 3 and 4.5 Å⁻¹. The strongest peak around 3.7 Å⁻¹ is the bixbyite (440) reflection, which appears for the ex situ diffraction at 2θ of about 55°. At time 0, the sample is exposed to synthetic air at 150°C. Shortly, the bixbyite reflections are seen to move slowly to lower q, indicating lattice expansion that is nearly isotropic. Peaks shown that do not shift are reflections from the sample holder stage. Some weakening in the intensity of those peaks is observed, which may indicate very slight movement of the sample due to thermal expansion of the sample holder during oxidation. We also observe that reflection peaks for the Mn-doped samples are much broader, consistent with ex situ observations showing Mn-doped samples have poorer crystallinity than their Ti-doped counterparts. Notably, the Ti-doped sample in panel b shows a splitting of the
peak after about 25 minutes of oxidation. This splitting is attributed to the phase transformation of bixbyite \( V_2O_3 \) to form rutile \( VO_2 \), as discussed above. By contrast, the peak shifts to lower q for the Mn-doped case are not accompanied by formation of any new crystalline impurity phases. Rather, this transition is partially reversible upon heating to 300°C under nitrogen. Unabridged \textit{in situ} diffraction for the oxidation and reduction of the Mn:V\(_2\)O\(_3\) nanocrystals is shown in Figure S6, and for the full q range collected of oxidation of the Ti:V\(_2\)O\(_3\) nanocrystals in Figure S7. All the V\(_2\)O\(_3\) samples show a lattice expansion upon oxidation, as evidenced by bixbyite peaks moving to lower q during oxidation. Scherrer analysis of the (222), (440), and (622) reflections was conducted before, during, and after oxidation to assess the extent of lattice expansion. In the fully oxidized state, Ti-doped nanocrystals showed a 1.3% expansion, while Mn-doped nanocrystals showed 1.6% expansion, compared to 0.6% expansion for undoped V\(_2\)O\(_3\) seen in a previous study.\(^3\) The main difference in these two doped materials appears to be their degradation mechanism during repeated cycling. These observations support the conclusion that doped V\(_2\)O\(_3\) nanocrystals follow two different degradation mechanisms depending on the dopant. For Mn-doped materials, oxidation causes disordering of the crystalline structure to form amorphous vanadates and manganates, which have much less storage capacity than the original vanadium oxide lattice. In contrast, Ti-doped materials experience an irreversible phase transition to monoclinic \( VO_2 \) during oxidation that causes loss in OSC. This difference may be due to the Ti\(^{4+}\) dopant’s positive relative charge, which may stabilize oxygen interstitials, facilitating a transformation to the higher oxidation state vanadium oxide.

\textbf{Conclusions}

Vanadium sesquioxide nanocrystals were synthesized with titanium and manganese dopants. These are incorporated as aliovalent dopants Ti\(^{4+}\) and Mn\(^{2+}\). Doped materials were compared to
the undoped by thermogravimetric analysis. Cycling these materials between oxidation and reduction ten times revealed that cycling these oxygen storage materials results in degradation of the oxygen storage capacity. This degradation is driven primarily by the irreversible oxidation of the materials during the low temperature oxidation step. Furthermore, we have found that Mn-doped and Ti-doped V2O3 nanocrystals degrade by different mechanisms. For undoped and Mn-doped materials, the nanocrystals tend to degrade by amorphizing the initially crystalline bixbyite phase material to form an impurity phase of inactive amorphous material. For Ti-doped V2O3, there is an additional degradation method in which the nanocrystals undergo irreversible phase transition to form rutile VO2 during oxidation, perhaps promoted by Ti4+, which may promote filling of oxygen vacancies because of its charge imbalance and the fact that Ti itself forms a rutile oxide. This degradation progresses over all ten cycles, resulting in an OSC that declines approximately linearly with cycle number. Aliovalent dopants may drive degradation products to a structure that the oxide of the dopant shares with a vanadate or to amorphous materials in case no favorable crystalline polymorph exists between the dopant and vanadium oxide. Future work might therefore seek a dopant that shares a structure with a vanadate which is a stable oxygen deficient structure. Cerium and indium may be prime candidates for this, since cerium oxide is a known oxygen ion conductor and indium shares the bixbyite structure in common with vanadium sesquioxide.

Methods

Material Synthesis

Doped bixbyite-phase vanadium sesquioxide materials were synthesized by modifying the reported vanadium sesquioxide nanocrystal synthesis, replacing some amount of vanadyl acetylacetonate with an equimolar amount of a metal dopant precursor. For the titanium-doped samples, the metal dopant precursor was Ti (IV) oxyacetylacetonate. For the manganese-doped
samples, the precursor was Mn (II) acetylacetonate. Nominal dopant percentages indicate the percent of vanadyl acetylacetonate that was replaced with the dopant metal precursor. Synthesis was done with 1 mmol of metal precursor, 4 mmol oleic acid, 4 mmol oleylamine, and 8 ml squalene. Chemicals were loaded into a 50 ml round-bottom 3-neck flask and degassed under dynamic vacuum at 110°C for an hour before switching to a nitrogen atmosphere and increasing the temperature to the synthesis temperature of 370°C. This temperature was held for 1 hour before cooling to room temperature. Nanocrystals were washed several times with isopropanol and hexane before use or characterization. Solutions were washed and stored air-free, powder or dry samples stored in nitrogen or in a vacuum dessicator.

Thermogravimetric Analysis

TGA was collected with a Mettler Toledo TGA 2. Samples were dropcast from solution into 100 ul aluminum crucibles and allowed to dry. Multiple depositions were used until the total weight of sample in the crucible was between 5 and 10 mg.

Inductively Coupled Plasma Atomic Emission Spectroscopy

Doped and undoped samples were digested with 70% nitric acid and diluted to contain 2% nitric acid. ICP AES was collected using a Varian 720-ES ICP AES.

Transmission Electron Microscopy

TEM images were obtained using a JEOL 2010F electron microscope equipped with a Schottky field emission gun and a CCD camera, operated at 200 kV.

X-ray Photoemission Spectroscopy

As-synthesized colloidal particles were dropcast onto p-type doped silicon substrates, and X-ray photoemission was collected with a Kratos Axis Ultra DLD spectrometer with a monochromatic Al Kα source (1486.6 eV). Resulting spectra were analyzed with CasaXPS equipped with the
Kratos library of elemental relative sensitivity factors. Spectra were treated with a simple constant correction to calibrate the main carbon 1s peak to an energy of 284.8 eV.

**X-ray Diffraction**

*In situ* X-ray diffraction of doped vanadium sesquioxide materials was performed at the Stanford Synchrotron Radiation Lightsource in Stanford, California. Using the Anton Paar *in situ* heating cell, powder samples of vanadium sesquioxide materials deposited on silicon substrates were irradiated with an X-ray beam with an energy of 14 eV. The diffraction image was collected with a Pilatus 300k detector in landscape orientation and analyzed using the Nika and Irena X-ray analysis package with Igor. The sample was reduced *in situ* under constantly flowing nitrogen gas at 300°C for one hour before the experiment began, to remove any adventitious carbon or water on the sample’s surface. The sample was then cooled to 50°C in nitrogen, at which point the flowing gas was changed to a synthetic air mixture. In the air atmosphere, the sample was heated slowly from 50°C to 150°C and held at 150°C for one hour. Then the gas was switched to nitrogen and the sample was heated to 300°C and held at 300°C for one hour.

*Ex situ* X-ray diffraction measurements were obtained using a Rigaku R-Axis Spider diffractometer with a Cu sealed tube source and a large, image plate detector.

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