Monodisperse Samarium and Cerium Orthovanadate Nanocrystals and Metal Oxidation States on the Nanocrystal Surface

Thanh-Dinh Nguyen, Cao-Thang Dinh, and Trong-On Do*

Department of Chemical Engineering, Laval University, Quebec G1K 7P4, Canada

Received April 19, 2009. Revised Manuscript Received May 31, 2009

A new solvothermal method has been developed for the synthesis of monodisperse SmVO₄ and CeVO₄ nanocrystals with controlled size and shape. The obtained materials were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) techniques. The results reveal that uniform nanocrystals and pure tetragonal phase of SmVO₄ and CeVO₄ can be achieved. To investigate the oxidation states of the metals on the mixed oxide nanocrystal surface, the XPS technique was employed. The results exhibit that only one oxidation state of samarium, cerium, and vanadium for each metal (e.g., Sm³⁺, Ce⁴⁺, V⁵⁺) is surprisingly well stable on the particle surface at the nanoscale, even after calcination, while the existence of two oxidation states of these metals is observed (e.g., Sm³⁺/Sm⁵⁺, Ce³⁺/Ce⁴⁺, V⁵⁺/V⁴⁺) in the corresponding single metal oxide nanocrystals.

1. Introduction

Rare earth orthovanadate (Re−V−O) crystals have potential applications as catalysts and support owing to their high surface area, thermal stability, and oxygen storage/release capacity (OSC). These materials have been used as oxygen ion conductors in solid oxide fuel cells, as three way catalysts (TWCs), and as high-activity catalysts in oxidative dehydrogenation of propane to propene and selective oxidation of hydrogen sulfide to sulfur in aqueous solutions. Recently, different shapes and sizes of these monodisperse mixed oxide NCs can be obtained using this approach. Although several methods have been reported, to the best of our knowledge, up to date, few studies have been focused on the synthesis of uniform SmVO₄ and CeVO₄ nanocrystals. Furthermore, our method is fundamentally different from the previous methods for the synthesis of these types of materials in aqueous and organic solutions. The monodisperse SmVO₄ and CeVO₄ NCs obtained by our approach are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). The oxidation states of the metals in the lattice are examined by X-ray photoelectron spectroscopy (XPS) both before and after calcination, compared to those of the corresponding single metal oxide NCs (e.g., Sm₂O₃, CeO₂, V₂O₅).

2. Experimental Section

Starting Materials. All chemicals were used as received without further purification. Samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O, 99.9%), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99.9%), vanadium pentoxide (V₂O₅, 99.9%), tetraoctylammonium bromide ([CH₃(CH₂)₇]₄NBr or TOABr, ≥98%), potassium oleate (C₁₇H₃₄COOK or KOA, 40 wt % paste in water), and oleylamine (C₁₈H₃₇NH₂ or OM, tech. grade, 70%) were used as received.

11142 DOI: 10.1021/la901387q Published on Web 07/02/2009 Langmuir 2009, 25(18), 11142−11148
were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 97%) and all solvents used such as toluene and ethanol were of analytical grade and purchased from Reagent ACS.

**Synthesis of Rare Earth Orthovanadate (ReVO₄, Re = Sm and Ce) Nanocrystals.**

**Preparation of Re(OA)₃ Complexes.** To prepare rare earth olate complexes, an organic solution was produced from adding 40 mL of toluene into the ethanol solution (10 mL) containing potassium olate (KOA, 6.4 g or 0.008 mol). The organic solution was mixed with 30 mL of a Re(NO₃)₃·6H₂O aqueous solution (0.067 mol/L) with a Sm³⁺/OA⁻ molar ratio of 1:3 and then transferred to a flask. The two-phase mixtures were heated to 70 °C for 60 min with vigorous stirring, and the organic solution became light yellow after being reacted, indicating the occurrence of the coordinated reaction of Re³⁺ and OA⁻ for the complex formation. Subsequently, the upper deep orange supernatant toluene solution (40 mL) containing Re(OA)₃ complexes (0.059 mol/L) was isolated.

**Preparation of VO₄(TOA)₃ Complexes.** A total of 0.24 g (0.0013 mol) of commercial bulk V₂O₅ powders was dissolved in 20 mL of a 0.12 M NaOH aqueous solution and vigorously stirred at room temperature for 30 min. V₂O₅ powders were completely dissolved in the dilute NaOH solution to give a homogeneous light orange Na₃VO₄ aqueous solution (~0.133 mol/L). Then, 40 mL of toluene solution (0.040 mol/L) containing a cationic phase-transfer reagent ([CH₃(CH₂)₇]₄NBr or TOABr, 0.87 g) was added to the above solution, and the VO₄⁻/TOA⁺ molar ratio was close to 1:3. The two-phase mixture was vigorously stirred at room temperature. After 30 min, VO₄⁻ anions in the aqueous phase were completely extracted into the toluene phase, and a light orange toluene solution was observed. Subsequently, the upper light orange supernatant toluene solution (40 mL) containing VO₄(TOA)₃ complexes (0.059 mol/L) was isolated.

**Synthesis of ReVO₄ Nanocrystals.** Typically, the two above toluene solution containing Re(OA)₃ complexes and VO₄(TOA)₃ complexes (0.059 mol/L) were mixed together with a Re/V molar ratio of close to 1:3. The two-phase mixture was vigorously stirred at room temperature. After 30 min, VO₄⁻ anions in the aqueous phase were completely extracted into the toluene phase, and a light orange toluene solution was observed. Subsequently, the upper light orange supernatant toluene solution (40 mL) containing VO₄(TOA)₃ complexes (0.059 mol/L) was isolated.

**Characterization.** The particle sizes and morphologies of the synthesized samarium and cerium orthovanadate nanocrystals were determined at 120 kV by using a JEOL JEM 1230 transmission electron microscope. Samples were prepared by placing a drop of a dilute toluene dispersion of nanocrystals onto a 200 mesh carbon coated copper grid and immediately evaporated at ambient temperature. Particle size distribution diagrams were obtained from statistical treatment of representative TEM images of each sample by measuring the diameter of typically not less than 300 particles using the software ImageJ. Average particle diameters were determined from these size distribution diagrams. The crystalline phases of products were characterized on a Bruker SMART APEXII X-ray diffractometer operated at 1200 W power (40 kV, 30 mA) to generate Cu Kα radiation (λ = 1.5418 Å). The XPS spectra were taken on a photoelectron spectrometer (KRATOS AXIS-ULTRA) with a monochromatic X-ray source of Al Kα. The operating conditions for recording Sm 3d, Ce 3d, V 2p, O 1s, C 1s, and N 1s high-resolution spectra were 1486.6 eV and 225 W, pass energy of 160 eV with an operating pressure of 10⁻⁹ Torr, acquisition time of 5.75 min, and a pressed mixed oxide pellet under an Ar⁺ bombardment. 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. The UV–vis spectra of the as-synthesized ReVO₄ nanocrystals were recorded on a Hitachi U-3100 spectrometer, and pure MgO was used as a blank. The thermal analyses of the as-synthesized ReVO₄ nanocrystals were repeated several times to purify the producing ReVO₄ nanocrystals.


---

**Scheme 1. Schematic Illustration for the Formation of the Re(OA)₃ and VO₄(TOA)₃ Complexes (i) and the ReVO₄ Nanocrystals (ii)**
**3. Results and Discussion**

The synthesis of ReVO₄ nanocrystals consists of two steps: (i) the preparation of Re(OA)₃ complexes (Re = Sm and Ce) and VO₄(TOA)₃ complexes from inexpensive precursors; Re(NO₃)₃ and V₂O₅ powders, respectively; (ii) the formation of ReVO₄ nanocrystals (e.g., SmVO₄ and CeVO₄ NCs) from the presynthesized Re(OA)₃ and VO₄(TOA)₃ complexes. The formation of ReVO₄ NCs is schematically illustrated in Scheme 1, and detailed synthesis of these materials is reported in the Experimental Section. Metal oxide nanocrystals of Sm₂O₃, CeO₂, and V₂O₅ were also synthesized following the methods reported previously by our group.²⁴-²⁶

Figures 1 and 3 show the X-ray diffraction (XRD) patterns of the as-made SmVO₄ and CeVO₄ nanocrystal samples, respectively. All the XRD peaks are well indexed to tetragonal zircon-type structure with the following lattice contents: SmVO₄: \( a = b = 7.265 \text{ Å}, c = 6.389 \text{ Å} \) (Fm\( \overline{3} \)m, JCPDS card no. 17-0876);³⁺ CeVO₄: \( a = b = 7.265 \text{ Å}, c = 6.389 \text{ Å} \) (I\( \overline{1} \)amd, JCPDS card no. 12-0757).³⁻ The intense broadening of the peaks is caused by the small particle sizes. The average crystalline size of these as-made SmVO₄ and CeVO₄ NC samples calculated from the broadening of the (200) peak using the Scherrer formula are 17.5 and 18.5 nm, respectively. Furthermore, for the corresponding as-made single metal oxide NCs, the XRD patterns exhibit cubic phase (JCPDS card no. 78-0429) for Sm₂O₃,²⁴ cubic phase (JCPDS card no. 78-0429) for CeO₂,²⁶ and orthorhombic phase (JCPDS card no. 78-0429) for V₂O₅ (Supporting Information S-Figure 1).²⁵ Their XRD peaks did not match at all those of the mixed oxide SmVO₄ and CeVO₄ NCs. Otherwise, no XRD peaks of the SmVO₄ and CeVO₄ NC samples which correspond to single metal oxide NCs of Sm₂O₃, CeO₂, and V₂O₅ were detected, indicating that the pure tetragonal zircon-type structure of SmVO₄ and CeVO₄ NCs can be achieved by this method. It can be also concluded that the formation of the pure tetragonal ReVO₄ phase results in the.

---

complete reaction of the 1:1 ratio of Re$^{3+}$ cation and VO$_4^{3-}$ anion monomers in the bulk solution during the synthesis.

The shape of SmVO$_4$ and CeVO$_4$ NCs could be controlled by the synthesis temperature. TEM images, SEAD patterns, and particle size distribution (PSD) diagrams of the samples synthesized solvothermally at 150 and 180 °C for 16 h are shown in Figures 2 and 4. Nearly cubic-shaped SmVO$_4$ and round-shaped CeVO$_4$ nanocrystals with an average diameter of 15 nm were found at 150 °C. When the synthesis temperature increased to 180 °C for 16 h, both uniform SmVO$_4$ and CeVO$_4$ nanospheres were observed; however, the diameter is unchanged. A slight change in color of the toluene containing nanoparticles from light yellow to brown was observed, when the reaction temperature was increased from 150 to 180 °C, indicating a change in shape of the nanoparticles (Supporting Information S-Figure 3). The inset SAED patterns taken from single particles are also indexed to a tetragonal SmVO$_4$ and CeVO$_4$ single crystal with strong ring patterns from the (200), (112), (301), (312), and (420) planes which are consistent with the XRD results. PSD diagrams of these samples were obtained from the statistical treatment of particle diameters from representative TEM images, indicating a change in shape from cubic to spherical NCs (Supporting Information S-Figure 3). The PSD becomes narrower, indicating more uniform nanoparticles, when the reaction temperature is increased from 150 to 180 °C. The transformation of both cubic-shaped SmVO$_4$ and round-shaped CeVO$_4$ NCs into uniform nanospheres while preserving the particle size by increasing synthesis temperature from 150 to 180 °C can be explained by the Wulff facets theory. Because no monomer precursors were added during the synthesis, at the relatively low reaction temperature (e.g., 150 °C), the cubic-shaped SmVO$_4$ and round-shaped CeVO$_4$ nanocrystals were formed in the anisotropic growth of high-energy crystal faces owing to high monomer metal concentration in bulk solution. The differences in cubic and round shapes of the SmVO$_4$ and CeVO$_4$ nanocrystals, respectively, could be due to the different nature of their corresponding rare earth metals. At higher synthesis temperature (e.g., 180 °C), the transformation of both the cubic- and round-shaped nanocrystals into uniform nanospheres could be explained by the depletion of remaining metal monomer concentration in bulk solution to a level lower than that required for a given anisotropic shape. Consequently, the monomers of the dissolved crystals at high energy faces could move to the lower energy faces because of the differences in chemical potential between different crystal faces. As a result, the corners and the tips of the cubic-shaped SmVO$_4$ and round-shaped CeVO$_4$ nanocrystals were “smoothed”, which leads to the formation of stable nanospheres with a minimum face energy.

The UV–vis absorption spectra of the as-made SmVO$_4$ and CeVO$_4$ nanosphere samples are shown in Figure 5. A strong absorption peak at 265 and 264 nm for the SmVO$_4$ and CeVO$_4$ samples, respectively, is observed, which is attributed to the charge transfer from the oxygen ligands to the central vanadium.

Figure 4. TEM images of 15 nm sized CeVO$_4$ nanocrystals synthesized at different temperatures for 16 h: (a) round-shaped nanocrystals at 150 °C and (c) corresponding particle size distribution; (b) nanospheres at 180 °C (inset, SAED) and (d) corresponding particle size distribution.
atom inside the V\(\text{O}_3\) groups in the samarium and cerium orthovanadate, respectively. However, no significant change in the position of this peak was observed with different shapes of these samples. This could be due to almost the same of the nanoparticle size (\(\sim 15 \text{ nm}\)).

The thermogravimetric analysis/differential thermal analysis (TGA–DTA) curves (Figure 6) of the oleylamine (OM)-capped Sm\(\text{V}\text{O}_4\) and Ce\(\text{V}\text{O}_4\) nanospheres exhibit the weight loss of 22 and 21\% appearing around 150–300 °C accompanied by the exothermic peaks at 305 and 248 °C, respectively, which are related to the decomposition and combustion of oleylamine molecules on the particle surfaces upon heating. The exothermic peaks of both samples occur at the different two temperatures which can result from the different binding of oleylamine molecules to their corresponding nanocrystal surfaces. The FTIR spectra (Figure 7) of these OM-capped samples show at 2920–2870 cm\(^{-1}\) which are assigned to the C–H stretching modes of alkyl chains in oleylamine. The band at 1440 cm\(^{-1}\) is attributed to the N–H bending and N–C stretching modes of \(-\text{NH}_2\) groups in oleylamine capped on nanocrystal surfaces. The IR band at 810 cm\(^{-1}\) is attributed to the \(\text{Re–O–V}\) vibrations of Re\(\text{V}\text{O}_4\). Residual water and a hydroxide group are detected with a large band around 3450 cm\(^{-1}\), corresponding to the O–H stretching frequency due to the bending vibration of associated water. These data suggest that oleylamine molecules were bound to the nanocrystal surface and further confirm that Sm\(\text{V}\text{O}_4\) and Ce\(\text{V}\text{O}_4\) were formed under these synthetic conditions.

The metal oxidation states on the particle surface of the Sm\(\text{V}\text{O}_4\) and Ce\(\text{V}\text{O}_4\) NCs and corresponding single metal oxides (e.g., Sm\(\text{O}_3\), Ce\(\text{O}_2\), V\(\text{O}_5\)) were examined by XPS. The survey XPS spectra of these as-made and calcined mixed oxide NC samples in a wide energy range are presented in S-Figures 3 and 4 in the Supporting Information; beside 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 samples can be assigned to the oleylamine ligand capped on the NC surface. The positions of XPS peaks were corrected using the C 1s core level taken at 285 eV as a binding energy (BE) reference. Surprisingly, the Sm 3d, Ce 3d, and V 2p XPS spectra of both the as-made and calcined Sm\(\text{V}\text{O}_4\) and Ce\(\text{V}\text{O}_4\) nanospheres exhibit only one oxidation state for each metal (e.g., Sm\(^{3+}\), Ce\(^{3+}\), V\(^{5+}\)) at the nanoscale and even in ultrahigh vacuum for XPS measurements (see Figures 8 and 9). The Sm 3d\(5/2,3/2\) peaks at 1083.5–1110.8 eV, the Ce 3d\(5/2,3/2\) peaks at 885.7–904.0 eV, and the V 2p\(3/2,1/2\) peaks at 517.2–525.5 eV attributed to Sm\(^{3+}\), Ce\(^{3+}\), and V\(^{5+}\), respectively, were observed. No peaks characteristic of other metal oxidation states of these metals were detected. However, for the single NC samples of samaria, ceria, vanadia, the Sm 3d, Ce 3d, and V 2p XPS spectra exhibit two additional weak peaks at 1095.9–1121.3 eV for Sm\(^{2+}\), Ce\(^{3+}\), and V\(^{5+}\).


Ce- and V4 Sm2 CeVO4 nanosphere samples. It means that, in these single metal oxides, the single SmO3, CeO2, and V2O5 NCs, and (c) calcined SmVO4 nanospheres, (b) calcined SmVO4 nanospheres, and (c) calcined CeVO4 nanospheres.

Figure 9. V 2p XPS spectra of the spherical NC samples: (a) as-made SmVO4 NCs, (b) calcined SmVO4 NCs, and (c) calcined V2O5 NCs.

Figure 8. (A) Sm 3d XPS spectra of (a) the as-made SmVO4 nanospheres, (b) the calcined SmVO4 nanospheres, and (c) the calcined Sm2O3 nanospheres. (B) Ce 3d XPS spectra of (a) the as-made CeVO4 nanospheres, (b) the calcined CeVO4 nanospheres, and (c) the calcined CeO2 nanospheres.

At 879.5–914.0 eV for Ce3+ 3d5,2,3/2, and at 516.2–524.1 eV for V4+ 2p5,2,3/2, as compared to those of the mixed oxide SmVO4 and CeVO4 nanosphere samples. It means that, in these single metal oxide NC samples, these metals exist in two oxidation states, and the fit peaks revealed Sm3+ (60%) and Sm2+ (40%) for samarium,24 Ce4+ (54%) and Ce3+ (46%) for cerium,26 V5+ (65%) and V4+ (35%) for vanadium.25

The XPS results revealed that, for each metal, only one oxidation state (e.g., Sm3+, Ce4+, V5+) exists in the SmVO4 and CeVO4 NCs, and meanwhile, two oxidation states (Sm3+/Sm2+, Ce4+/Ce3+, V5+/V4+) in the single Sm2O3, CeO2, V2O5 NCs were found. This difference is due to the fact that, for each single metal oxide, the single Sm−O−Sm bonds in Sm2O3, the Ce−O−Ce bonds in CeO2, and the V−O−V bonds in V2O5 allow the multiple oxidation states, whereas, for the mixed metal oxides, the presence of mixed Sm−O−V bonds in SmVO4 and Ce−O−V bonds in CeVO4 requires the formation of Sm3+−V5+, and Ce3+−V4+ species, respectively.32,33 In fact, the formation of the ReVO4 phase (Re=Sm and Ce) results in the interaction between the nuclear spin of the V atom and unpaired 4f electron of Re. Fermi contact interaction could be involved with the transfer of the unpaired 4f electron of the Re ions to the orbital on the V atom,34−36 and hence a slight chemical shift to a higher binding energy (shifted ∼0.3−1.3 eV) of Sm 3d, Ce 3d, and V 2p of ReVO4 NCs compared with that of Sm2O3, CeO2, and V2O5 NCs.3,37 As a result, V and Re possess a valence of +5 and +3, respectively, in the ReVO4 lattice.

For the CeVO4 NCs, as seen in Figure 10a, the O 1s peak at 530.2 eV is attributed to both O−Re and O−V bonds in the tetragonal ReVO4 lattice31 which consists of VO4 tetrahedra which share corners and edges with ReO8 dodecahedra,15,17 and another shoulder peak at 532.2 eV could be associated with a Sm Auger peak (∼526.8 eV).38,39 The XPS analysis confirms that the molar ratio of Re/V in these samples is very close to 1:1, agreeing with the formula of ReVO4.

their mobility on the metal oxide surface at reaction temperature are of great importance for redox reactions.\textsuperscript{35,40,41} Further work to determine the amount of oxygen released of both lattice oxygen and adsorbed oxygen species from these mixed oxide NCs using the TPD-O\textsubscript{2} technique as well as the nature of oxygen species involved in catalytic oxidation is in progress in our laboratory.

4. Conclusions

We have developed a simple and reproducible method for the synthesis of uniform SmVO\textsubscript{4} and CeVO\textsubscript{4} nanocrystals from the solvolysis of a mixture of Re(OA)\textsubscript{3} (Re = Sm and Ce) and VO\textsubscript{4}(TOA)\textsubscript{3} complexes in toluene in the presence of oleylamine ligand. By increasing the reaction temperature from 150 to 180 °C, SmVO\textsubscript{4} and CeVO\textsubscript{4} NCs can converted from cubic-shaped SmVO\textsubscript{4} and nearly round-shaped CeVO\textsubscript{4} to uniform nanospheres. The XPS results revealed that only one oxidation state of samarium, cerium, and vanadium for each metal (e.g., Sm\textsuperscript{3+}, Ce\textsuperscript{3+}, V\textsuperscript{5+}) exists in the mixed oxide spherical NCs, SmVO\textsubscript{4} and CeVO\textsubscript{4}, while two oxidation states for each metal (Sm\textsuperscript{3+}/Sm\textsuperscript{2+}, Ce\textsuperscript{4+}/Ce\textsuperscript{3+}, V\textsuperscript{5+}/V\textsuperscript{4+}) exist in the corresponding single metal oxide spherical NCs, Sm\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, and V\textsubscript{2}O\textsubscript{5}. Our synthetic approach could also be useful for the synthesis of other uniform rare earth orthovanadate, molybdate, and tungstate nanocrystals as well as doped NCs and multicomponent NCs.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through a strategic grant.

Supporting Information Available: XRD patterns, TEM images, corresponding SAED patterns, and survey XPS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

Monodisperse Samarium and Cerium Orthovanadate Nanocrystals and Metal Oxidation States on the Nanocrystal Surface

Thanh-Dinh Nguyen, Cao-Thang Dinh, and Trong-On Do*

Department of Chemical Engineering, Laval University, Quebec G1K 7P4 Canada

To whom correspondence should be addressed. E-mail: Trong-On.Do@gch.ulaval.ca

SUBMITTED TO Langmuir – April 2009

Supporting Information

S-Figure 1. XRD patterns of the calcined single metal oxide spherical NCs: (a) Sm$_2$O$_3$, (b) CeO$_2$, (c) V$_2$O$_5$. 

S-1
S-Figure 2. TEM images and corresponding inset SAED patterns of the as-made single metal oxide spherical NCs: (a) Sm₂O₃, (b) CeO₂, (c) V₂O₅.
S-Figure 3. TEM images of the 15 nm ReVO₄ nanocrystal samples and color photographs of the transparent toluene solution containing oleylamine-capped nanocrystals synthesized solvothermally at different temperatures for 16 h:

- SmVO₄: (a) nanocubes at 150 °C, (b) nanospheres at 180 °C, and their corresponding photograph (inset).
- CeVO₄: (c) round-shaped nanocrystals at 150 °C, (d) nanospheres at 180 °C, and their corresponding photograph (inset).
**S-Figure 4.** Survey XPS spectra of the as-made SmVO₄ nanospheres obtained before (a) and after (b) calcination at 550 °C for 2 h.

**S-Figure 5.** Survey XPS spectra of the as-made CeVO₄ nanospheres obtained before (a) and after (b) calcination at 550 °C for 2 h.