Inhomogeneous depletion of oxygen ions in metal oxide nanoparticles

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ABSTRACT

Zirconia and yttria stabilized zirconia (YSZ) have multiple uses, including catalysis, fuel cells, dental applications, and thermal coatings. We employ nuclear reaction analysis to determine elemental composition of YSZ nanoparticles synthesized by laser evaporation including ^{18}O studies to distinguish between oxide and adsorbed oxygen content as a function of surface area. We see dramatic deviation from stoichiometry that can be traced to loss of oxygen from the oxide near the surface of these nanopowders. Density functional calculations are coupled with these experimental studies to explore the electronic structure of nonstoichiometric surfaces achieved through depletion of oxygen. Our results show oxygen-depleted surfaces present under oxygen potentials where stoichiometric, oxygen-terminated surfaces would be favored thermodynamically for crystalline systems. Oxygen depletion at nanopowder surfaces can create effective two-dimensional surface metallic states while maintaining stoichiometry in the underlying nanoparticle core. This insight into nanopowder surfaces applies to dissimilar oxides of aluminum and zirconium indicating synthesis conditions may be more influential than the inherent oxide properties and displaying need for distinct models for nanopowders of these important engineering materials where surface chemistry dominates performance.

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1. Introduction

Physical and chemical properties of oxide nanopowders and methods for their synthesis have been the subject of numerous studies. These appear in diverse fields, including catalysis, medicine, and electrochemical devices. In addition to practical applications, such studies hold fundamental implications for understanding the surface physics and chemistry of oxide materials as well as the nature of their magnetic and electronic properties. An important characteristic of oxide nanopowders is their chemical composition. Of particular interest is deviation from stoichiometry and the extent and location of oxygen vacancies in nanoparticles since this presents dramatic consequences for the resulting electronic structure.

There is evidence of deviation from stoichiometry in nanoscale oxide semiconductors and dielectrics even though these exhibit stoichiometric composition in larger scale grains and crystalline solids. Generally, stoichiometric deviation is determined indirectly by characterizing ferromagnetic states in nanopowders or thin films of oxides containing no magnetic dopants. This effect has been observed in a variety of metal oxides, including TiO_2, Al_2O_3, CeO_2, ZnO, In_2O_3, HfO_2, CuO, and Cu_2O [1–10]. The authors of these studies speculate that ferromagnetism of nanoscale oxides is due to oxygen deficiency. The prevailing interpretation is that vacancies are formed in the oxygen sublattice of oxides located in the outer surface layer of nanoparticles or films, i.e., these results indirectly point to inhomogeneous distribution of oxygen ions in oxide nanoparticles.

In theory as well as practical application, direct measurements of oxygen content in nanopowders provides essential complement to the indirect evidence of oxygen-depleted surfaces. We used nuclear reaction analysis (NRA) to quantify elemental composition of aluminum oxide nanoparticles whose oxygen sublattice is enriched with ^{18}O isotope [11]. NRA is employed as an alternative to electron spectroscopy methods [12–15] which may require preparation of a clean and homogeneous surface with certified structure. Such ideal surfaces generally cannot be ensured in the examination of nanoparticles; they are difficult to prepare even for monocrystals. The indirect signatures suggesting oxygen deficiency localized to the outer atomic layers in Al_2O_3 nanoparticles comprised of γ, δ, and amorphous phase were confirmed directly in our previous work [11]. Earlier characterization of higher symmetry α-Al_2O_3 crystals, including low-energy electron diffraction [16], grazing incidence x-ray diffraction [17], dynamic scanning force microscopy [18], non-contact atomic force microscopy, and density functional theory (DFT) calculations [19–21], shows that an oxygen-deficient surface reconstruction can be achieved under appropriate pressure and temperature conditions and then persist at ambient conditions where that surface is not thermodynamically favored. This $\sqrt{31} \times \sqrt{31}R9°$ reconstruction is achieved through loss of two oxygen layers from the stoichiometric surface, i.e., two O_3 units from the "Al-O_3-Al-Al-O_3-Al…" surface.

Relaxation of the remaining surface aluminum results in a thin layer of effectively Al(111) over a stoichiometric Al_2O_3 substrate.

At present, there is considerable indirect evidence of stoichiometric deviation in oxide nanopowders but only in our previous alumina study was this quantified directly, including oxygen isotope concentrations. A fundamental understanding may inform surface synthesis and allow tunable properties and reactivity of nanocrystalline oxides. Analyzing other oxide systems is needed to inform discussion of relevant functional properties of oxide nanopowders and to determine the degree of generality of this effect in oxide nanoparticles. Accordingly, we examine the distribution of oxygen ions in nanoparticles of a dissimilar oxide, yttrium-stabilized cubic zirconium oxide (YSZ), with substantially different properties from those of the aluminum oxide examined previously [11]. YSZ and Al_2O_3 oxides have different crystal lattices and packing, their cationic sublattices contain transition versus non-transition metals, and the values of oxygen diffusion coefficients in these oxides differ by several orders of magnitude [22,23]. Both oxides are used extensively as engineering materials.

Oxygen deficiency in the oxide nanoparticles may be achieved through evaporation of oxygen from the oxide during high-temperature synthesis of nanopowders. Although as mentioned this had been observed and characterized for α-Al_2O_3(0001) crystalline surfaces in the $\sqrt{31} \times \sqrt{31}$R9° reconstruction, the direct evidence for a similar effect in γ-Al_2O_3 nanopowders was quantified by us only recently [11]. No similar reconstructions have been characterized for pure zirconia monocrystals, much less for YSZ samples. In the case of c-ZrO_2 and YSZ, crystalline defects are common and the surfaces challenging to characterize partly due to phase competition and the associated chemical differences with low-percentage addition of other metal oxides to stabilize the cubic phase of zirconia. Nevertheless, a number of studies have characterized the low-index surfaces of zirconia and related oxides in monoclinic, tetragonal, and cubic phase, which may convert to tetragonal in the absence of cubic-stabilizing additions [24–32]. Unlike alumina where single-aluminum termination is favored in the absence of hydrogen [33], DFT with associated thermodynamic and molecular dynamics predictions of crystalline tetragonal or cubic zirconia surfaces show stoichiometric oxygen-terminated (111) surfaces presenting "O-Zr-OO-Zr-O…" layering to be the most stable thermodynamically spanning all relevant oxygen partial pressures [31,34].

Accordingly, in crystalline samples, there is well-characterized evidence for oxygen-deficient surfaces of alumina but not of zirconia or YSZ. Nanopowders uniquely emphasize surface over bulk thermodynamics since more than ten percent of total atomic content can be comprised of surface or near-surface species in these samples, whereas for monocrystals the surface might be considered a "perturbation" of the bulk crystal. In terms of surface energies, the "Al (111)" monolayer over the Al-O_3-Al-Al-O_3-Al… α-Al_2O_3 (0001) surface may present a lower energy surface, with Al (111) surface energy estimated at ~1000 mJ m^{-2} [35], while α-Al_2O_3 (0001) is more than twice that value [36]. Conversely, the estimates for Zr (0001) of close to 2,000 mJ m^{-2} [37–40] are ~40% higher than for cubic or tetragonal ZrO_2 (111) [24,25,28]. Consequently, simple analysis based on clean surface energy estimates from monocrystals does not provide an explanation for why metal oxide nanopowders might prefer metal-enriched overlayers. Nonetheless, experimental evidence pointing to oxygen deficiency at the surfaces of these samples is fairly ubiquitous.

In this current study, we present direct evidence for oxygen loss from the surface layer of YSZ10 nanopowders. We synthesize a series of nanopowders enriched in ^{18}O with increasing specific surface area. These samples are characterized using X-ray diffraction (XRD). We quantify ^{16}O and ^{18}O content in nanopowders using NRA and analyze oxide oxygen content versus oxygen uptake post-synthesis. We examine the thermal stability of these nanopowder surfaces and, using density functional calculations, explore the impact of oxygen depletion on nanopowder surface and electronic structure.

2. Samples and methods

The nanopowder samples were produced by laser evaporation of a ceramic target. The initial material for preparing the target was commercial micropowder YSZ10 (ZrO_2–10 mol% Y_2O_3) or $Zr_{0.82}Y_{0.18}O_{2-\delta}$. XRD analysis identified cubic structure with lattice parameters of 0.5145 nm. The initial pellet compaction was performed in air at room temperature and produced pellets of 15 mm diameter with 10–15 mm thickness and a density 35–40% of the theoretical density. Before preparing the target pellet for laser evaporation, the oxygen sublattice of the initial micropowder was enriched with ^{18}O isotope. For this purpose, the initial powder was annealed for 24 hours at 800 °C and 1 atm oxygen pressure enriched with 80% ^{18}O isotope. The annealing was performed in an alundum tube containing the pellets pressed from the initial powder. After annealing, the NRA results indicated about 15% enrichment in ^{18}O isotope of the oxygen sublattice. The ^{18}O-enriched powder then was ground in a mortar made of zirconium oxide to a powder with a specific surface area of 2.2 m^2/g. This ^{18}O-enriched micropowder was pressed in air at room temperature to produce a 60 mm diameter target for use in laser evaporation preparation of the nanopowders.

A fiber ytterbium laser with 1 kW maximum power operating at an irradiation wavelength of 1.07 μm was used in the nanopowder synthesis. Laser evaporation of the ceramic target was performed in an inert atmosphere (argon or helium) to prevent oxygen isotope exchange during synthesis. We needed to produce samples over a wide range of specific surface area values to characterize behavior for different average particle sizes. Accordingly, the type of inert gas (argon or helium), gas pressure, and laser power were varied and both pulsed and continuous modes of laser irradiation of the target were used during synthesis. In pulsed mode, the pulse duration was 60 μs and the frequency was 5 kHz. Laser radiation was focused on the target using an Optoskand d25 f60/200 optical system, which provided a maximum laser power density on the target surface of 10^7 W/cm^2. Regular wear of the target during laser irradiation was achieved by rotating the target and by its reciprocating motion in the plane perpendicular to the laser beam axis.

The conditions for nanopowder synthesis, the values of their specific surface area S and average sizes of X-ray coherent scattering domains are listed in Table 1. The specific surface area of the powders was determined using the BET method [41]. According to transmission electron microscopy data, the nanopowders had narrow particle size distribution and contained no particles larger than 1 μm since the synthesis apparatus was equipped to remove larger particles. X-ray diffraction (XRD) analysis of the nanopowders was performed using a DISCOVER D8 (Bruker) diffractometer operating at 40 kV and 40 mA with Cu-K$_\alpha$ radiation (λ = 0.1542 nm) equipped with a graphite monochromator on a secondary beam and scintillation detector in the Bragg–Brentano configuration. Bruker software TOPAS-3 with Rietveld full-profile refinement was employed for the quantitative analysis. The average size of coherent diffraction domains (crystallite size) was estimated by using the Scherrer approach with a correction coefficient of 0.89.

The X-ray diffraction spectra in Fig. 1 indicated that all nanopowders and the initial micropowder were monophase with a cubic lattice. The diffraction line width monotonously increased with the specific surface area of the powders. The line shape shows that virtually no amorphous phase and microstresses were in the nanopowders.

In some cases, we used thermogravimetry to estimate the quantity of adsorbed oxygen-containing molecules in the nanopowders. Analysis was carried out on an NETZSCH STA409 thermal analyzer equipped with a quadrupole mass spectrometer. The powders were heated at a rate of 10 K/min while dry argon was passed through the chamber.

The NRA study was performed using a 2-MV Van de Graaff accelerator. In preparation for measuring average concentrations of isotopes ^{16}O and ^{18}O, the YSZ10 micro- and nanoparticles were pressed in an indium plate. Rutherford backscattering spectrometry measurements showed