Oxygen-deficient 1D-nano-metal oxides and their energy applications

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Metal oxides, with their extensive variety of electronic- and chemical-properties are invaluable for fundamental research and for technological applications alike. Oxygen vacancies in metal oxides alter the spatial distribution of atoms in the material, and thus, change their physical- and chemical-properties. We describe herein the formation, microstructure, and physical properties, of oxygen-deficient 1D ceria, titanium, and the non-stoichiometric Magnéli phases in Ti_nO_{2n-1} nanorods. We discuss the potential energy applications of these forms of the materials, for example, in lithium ion batteries, and in the water-gas shift (WGS) reaction.

One important applications of the WGS reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is to minimize the CO content in fuel before it enters the main fuel-cell reaction chamber in a hydrogen car. [1-2] Oxygen-deficient ceria (CeO_{2-x}) is a promising candidate because it readily produces oxygen vacancies in an oxygen-deficient environment by reducing some Ce^{4+} ions to Ce^{3+} ions in the stable fluorite structure.

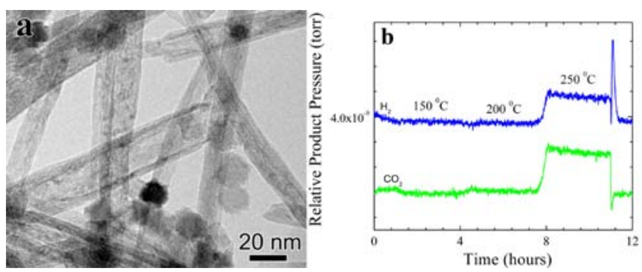

Figure 1(a) TEM image of 1D ceria; (b) WGS activity of pure ceria.

We synthesized polycrystalline 1D-nanostructural ceria by a hydrothermal method. [3] Before using it in the WGS reaction, we activated the 1D-ceria by pre-treating in pure H_2 up to 200 ºC. The *in-situ* time-resolved XRD patterns revealed the retention of the cubic-fluorite structure and average particle size of ceria during the reduction process, although there were major changes in the lattice parameters due to thermal expansion and partial reduction of the cerium oxide. We tested the activity of this pure reduced ceria, without adding any metal catalyst, in the NSLS' beam-line X7B at BNL. The WGS reaction was carried out isothermally in a flow cell at 150-200-, and 250- ºC. [4, 5] Figure 1b shows its WGS activity at 200 ^{o}C; it is increased further at 250 ºC. Interestingly, a large amount of H_2 was released when we lowered the temperature to room temperature naturally. This finding hints that CeO_2 is suitable for using as a host matrix for storing H_2.

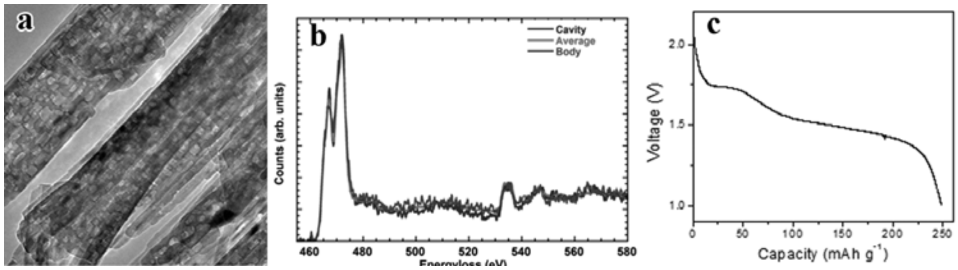

Figure 2(a) TEM image of TiO2 with nanocavities; (b) EELS spectra showing that oxygen deficiency at the inner surface of a nanocavity. (c) Voltage profile of lithium insertion into a TiO_2-nanocavity

We developed a new method to induce the formation of dense, regular nanocavities inside anatase nanorods. [6] Electron-energy-loss spectra show that both the outer-surface of these nanorods and the inner-surface of the nanocavities are oxygen-deficient (Figure 2(b)). We expect that these nanocavities will enhance Li-insertion capacity. Figure 2(c)) shows the voltage profile of lithium insertion into a-TiO_2 NRs with nanocavities. The capacity is close 250 mAh/g, i.e., higher than that for bulk anatase TiO_2 (167 mAh/g), and that for normal anatase nanorods (200 mAh/g). [7]

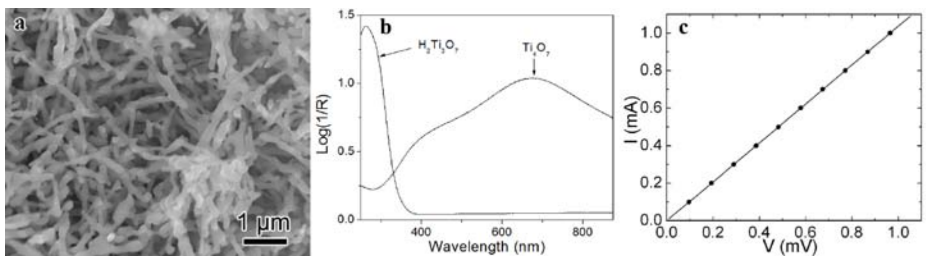

Figure 3(a) TEM image of Magnéli phases in Ti_nO_{2n-1} nanowires; (b) UV-vis diffuse reflectance spectra; (c) Room-temperature I-V curves of Ti_4O_7.

Anatase TiO_2 has poor internal electrical conductivity, so in applying it in Li-ion batteries, conductive carbon black must be added. We developed a novel method to make 1D Magnéli-phases Ti_nO_{2n-1} nanowires, consisting of n–1 TiO_2 octahedral and one TiO octahedral, and thus affected the material's optical- and electrical-conductivity. [8] The light absorption band of Magnéli phases Ti_nO_{2n-1} nanowires covers the full region of visible light, and extends into the near- IR region. The electrical conductivities of Ti_8O_{15} and Ti_4O_7 are, respectively, 0.24 S/cm, and 10.4 S/cm at 300 K. The high electrical-conducting behavior of the Magnéli phases Ti_nO_{2n-1} nanowires points to their potential employment as electrodes, which we soon will pursue.

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