Supplementary information

Facile Synthesis of Nanostructured Reduced Titanium Oxides Using Borohydride Toward the Creation of Oxide-Based Fuel Cell Electrodes

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Contents:

1. Experimental details

Instruments and measurements

- XRD: X-ray diffraction (XRD) patterns obtained using a RINT RAPID-Sdiffractometer (Rigaku, Tokyo, Japan) with an imaging plate by Cu Kα irradiation in transmission mode. The samples were packed in 0.2 mmφ Lindemann glass capillaries (Mark tube from Hilgenberg GmbH, Malsfeld, Germany), and the background was subtracted using the data obtained for an empty capillary.
- UV-vis-NIR: The diffuse reflectance spectra of the powder samples diluted with dry KCl powder to be 1 wt% were measured using a V-570 UV-vis-NIR spectrometer (JASCO, Tokyo, Japan) with an ISN-470 integrating sphere detector in the wavelength range from 2000 to 220 nm
- SEM: SU-8000 microscope from Hitachi High-Technologies, Tokyo, Japan. The images were obtained at 1.0 kV adjusted by the deceleration technology without coating the samples with conductors such as Pt and carbon.
- The cross-sectional transmission electron microscope (TEM) samples were prepared using the focused-ion beam and micro-sampling method on an FB-2100 FIB system (Hitachi High-Technologies, Tokyo, Japan). The TEM observation and electron energy loss spectroscopy (EELS) measurements were performed using a JEM-2100F microscope (JEOL, Tokyo Japan) at 200 kV.
- The temperature dependence of the resistance was measured from 8 to 300 K at ca. 1.2×10^{-5} Pa using a four probe method (bias: ±0.5 V) with a GRAIL 10-408040LV cryogenic electrical characteristic measurement system (Nagase Techno-Engineering, Tokyo, Japan) and a 4200-SCS semiconductor characterization system (Keithley Instruments, Tokyo, Japan). The reduced single crystals of (100)-oriented rutile TiO_2 were carefully cut into 2 mm × 5 mm pieces using the dicing saw. Then, four Au lines 100-μm wide (100-nm thick with a 10-nm Ti adhesion layer) were deposited by electron beam evaporation through a Si stencil mask. The width and length of the conduction pathway was defined by the mask. The thickness of the reduced region was measured by cross-sectional TEM observation of the fabricated samples using a focused ion beam.
- Electrochemical instrument: HZ-3000 from Hokuto Denko, Tokyo, Japan. The geometrical surface area of the working electrode was 0.46 cm^2.

Materials and chemicals

- $NaBH_4$: Reagent Grade from Kanto Chemical, Tokyo, Japan.
- TiO_2 single crystals: 10 mm × 10 mm, 0.5 mm thick crystals purchased from Furuuchi Chemical, Tokyo, Japan.
- TiO_2 nanorods: FTL-100 from Ishihara Sangyo, Osaka, Japan.
- H_2SO_4: Super Special Grade from Wako Pure Chemical Industries, Osaka, Japan.
- Water for electrochemistry: Millipore water.

2. Additional data

Table S1 Gibbs energy, ΔG, of the oxidation of four reducing agents

	$-\Delta G$ [a] / kJ mol^{-1}		
	25°C	350°C	1000°C
$NaBH_4$ (s)	313.7	321.9	338.3
CaH_2 (s)	377.5	384.3	398.0
NaH (s)	346.2	354.1	370.0
H_2 (g)	237.1	217.4	177.9

[a] These values were calculated using the standard Gibbs energies of formation and the standard entropies, for the formation of the most stable products at room temperature (without consideration on thermal decomposition of the hydrides): $4NaBH_4 + 8O_2 \rightarrow Na_2B_4O_7 + 2NaOH + 7H_2O$, $CaH_2 + O_2 \rightarrow Ca(OH)_2$, $2NaH + O_2 \rightarrow 2NaOH$, and $2H_2 + O_2 \rightarrow 2H_2O$. All the values were normalized for one oxygen atom.

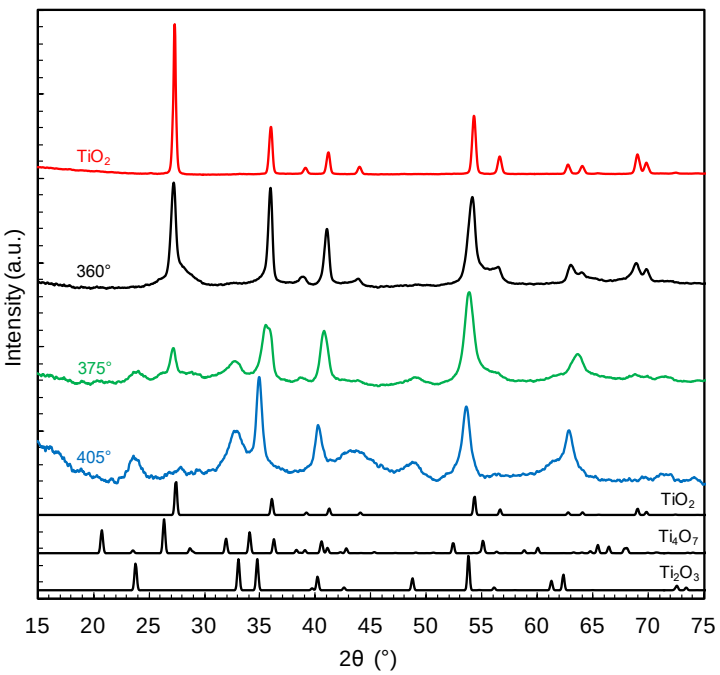

Figure S1 XRD patterns of rutile TiO_2 nanorods reduced using $NaBH_4$ at a different temperature for 24 h. Pressed pellets were formed from the TiO_2 powder mechanically mixed with the $NaBH_4$ powder, and then annealed in Ar. The three black patterns shown at the bottom are reported patterns of rutile TiO_2 (ICSD no. 9161), Magnéli phase Ti_4O_7 (no. 4813) and corundum Ti_2O_3 (no. 9646).

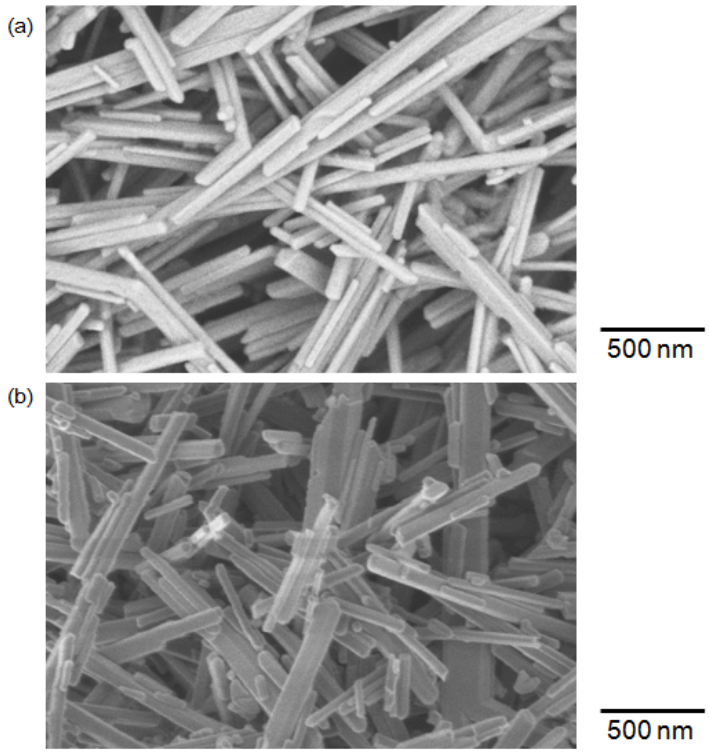

Figure S2 Low-voltage high resolution SEM image of the rutile-type TiO_2 nanorods reduced using $NaBH_4$ at 375°C for 24 h (a), compared with that of precursor TiO_2 (b). These images were obtained without surface coating.

3. Additional Acknowledgements

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