Supporting Information

Ultrafine Sodium Titanate Nanowires with Extraordinary Sr Ion-Exchange Properties

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Preparation of TiAl alloy ribbon

Highly-pure Ti (99.99%) and Al (99.99%) grain was melted with an electric arc-melting furnace in an Ar atmosphere. The atomic ratio of Ti : Al was 6 : 94. The alloy ribbons were prepared by the single-roller melt spinning that allow the rapid solidification of Ti_6Al_{94} alloy and the homogeneous distribution of $TiAl_3$ intermetallic compound nanocrystals in Al matrix. The thickness of the ribbons is measured to be about 20 μm.

Nanowire preparation

The Ti_6Al_{94} ribbon (750 mg) was treated in 300 mL of 5 M NaOH aqueous solution for 4 hours at room temperature. Visually, white turbid liquid dispersed by fine powders was formed. The powders were separated by centrifugation at 10,000 rpm for 1 min, and washed with 50 mM NaOH three times, and then rinsed with acetone. Finally, $NaTi_{1.75}O_4$ nanowire were dried in vacuum and the visual appearance is to be white fine powders (146 mg). The overall yield is 94%.

XRD, SEM, EDS, TEM, BET, and ICP-MS characterizations

Powder X-ray diffraction (XRD) measurements were performed by Rigaku SmartLab high-resolution X-ray diffractmeter. The rotating anode generator with Cu $K\alpha$ radiation was used. The tube voltage and current was 45 kV and 200 mA, respectively. JEOL JSM-6500FE scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS; Oxford Instruments, X-Max 50) was used for the microstructure characterizations. The JEOL JEM-2010F scanning/transmission electron microscopy (S/TEM) with an accelerating voltage of 200 kV equipped with EDS (Oxford Instruments, X-Max 80) was used for the nanostructure characterizations. By making the electron beam size converge down to approximately 1 nm in diameter, nano-beam diffraction patterns (NBDPs) were obtained to identify the crystal structures and crystallographic orientations of the nanowires. High-resolution TEM (HRTEM) images were taken by a FEI TITAN80-300 aberration-corrected TEM operated at an accelerating voltage of 200 kV. The BET specific surface area of the prepared samples was obtained by using Quantachrome Quadrasorb. The ICP-MS measurements were performed with Agilent 8800.

Sr^{2+} and Ba^{2+} adsorption experiments

The aqueous solution of $SrCl_2$ or $BaCl_2$ (4 mL) with given concentrations was added to the sodium titanate (4 mg) at room temperature at the desired pH, which was controlled by addition of 1 M HCl or 1 M NaOH. After the mixture was stirred for the required time, the adsorbent was separated by centrifugation at 10,000 rpm for 1 min, and washed with distilled water two times and acetone two times. The concentration measurement of the solution and the elemental analysis of the adsorbent were conducted with ICP-MS.

Figures

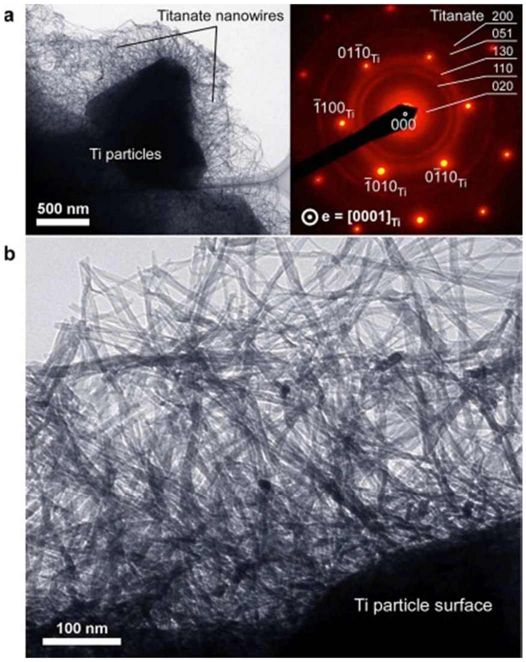

Figure S1. Nanostructures of sodium titanate nanowires prepared by immersing a “pure Ti” in NaOH solution. a, Bright-field TEM image (left) and selected-area diffraction pattern (right) of pure Ti powders after the treatment in 5 M NaOH aqueous solution for 4 hours at room temperature. The TEM image reveals that the nanowires with the three-dimensional network structures are formed only on the Ti surface. This indicates that the oxidization is not completed due to the kinetic limit. The diffraction rings reveals the layered structure in nanowire. b, Bright-field TEM image magnified the nanowires formed on the Ti surface. The observed nanowires have the diameters varied from 5 nm to 30 nm and remain tightly tangled in the vicinity of the Ti surface, forming the passivation layers during the reaction in NaOH.

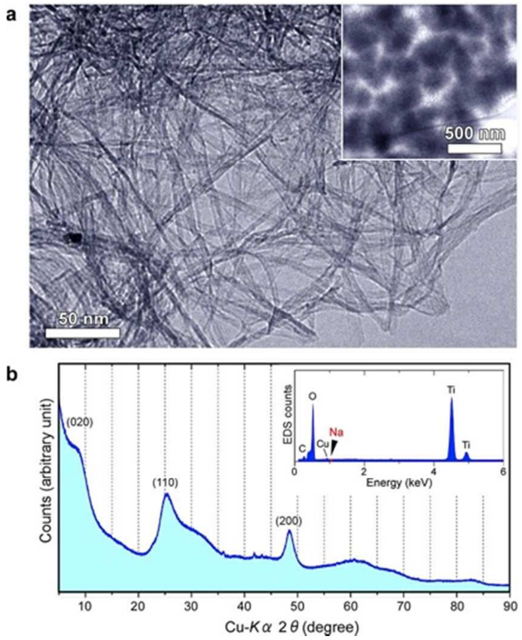

Figure S2. Nanostructures of ultrafine hydrogen titanate nanowires. a, Bright-field TEM images of hydrogen (protonated) titanate nanowires in 0.1 M HCl treatment of the original sodium titanate nanowires (see Figure 2a). The inset shows TEM image at lower magnification. It is noted that the hierarchical 3D-network structures are maintained after the HCl treatment. b, XRD profile and TEM-EDS spectrum (inset) of the H^+-exchanged nanowires. The EDS analysis reveals that the intercalated Na^+ in the layered titanate is disappeared and could be exchanged completely with H^+ and/or molecule H_3O^+. The XRD profile is changed after H^+ exchange (see Figure 3a) and could be an evidence of forming the H^+-exchanged $Na_2Ti_2O_4(OH)_2$ titanate with intercalated H_3O^+ molecules,[1] of which structure has the lepidocrocite-type layered framework and is analogous to $Na_xTi_{2-x/4}\square_{x/4}O_4$. The increase of specific surface area by protonation can be explained by the interlayer space enlarged due to the above intercalation. In fact, the 2θ peak position corresponding to the (020)-oriented plane in the XRD is found to shift to the lower angle of about 8.8 degree after H^+-exchange, indicating the interlayer distance is expanded.

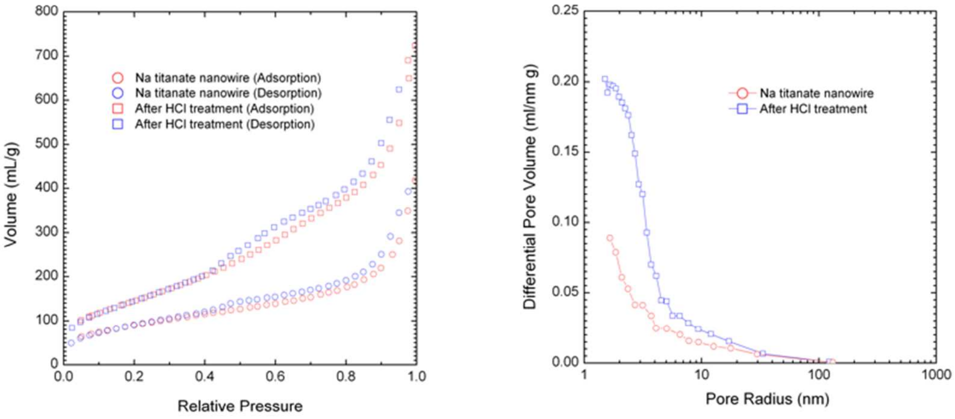

Figure S3. N_2 adsorption-desorption isotherms and BJH pore size distribution plots for before and after HCl treatment. a, N_2 adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distributions were measured. Before the measurements, the nanowires were washed by water, followed by acetone. Finally, they and were heated in vacuum at 423 K for 6 hours. According to IUPAC classification, the isotherm hystereses have been categorized four types of shapes.[2,3] The pores have nearly cylindrical channel with uniform size and shape (type H1) and with nonuniform size and shape (type H2). The pores have slit shaped pores with nonuniform size and shape (type H3) and with uniform size and shape (type H4). The obtained isotherm in Figure 1a corresponds to type H3, which is the existence of slit shaped pore with nonuniform size and shape. b, the BJH analysis indicates that there is no mesoporous and nanotubes.[4]

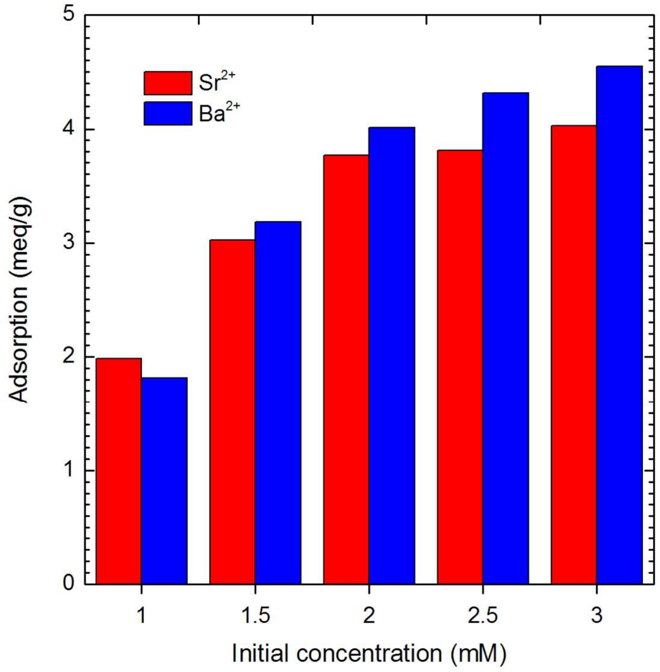

Figure S4. The adsorption of Sr^{2+} and Ba^{2+} with the sodium titanate nanowires. The vertical axis shows the uptake of ions in meq/g, while the horizontal axis indicates the initial concentration of ions.

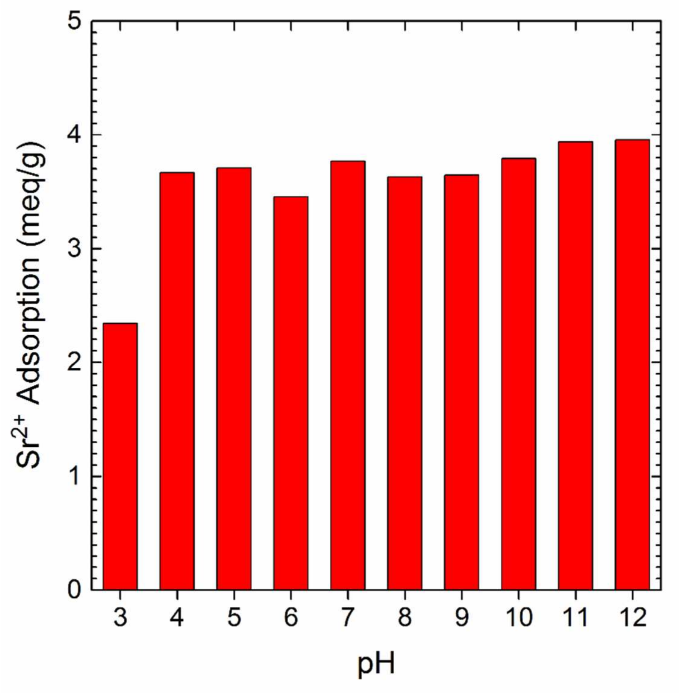

Figure S5. Dependence of pH on the Sr^{2+} adsorption in the nanowires. The vertical axis shows the uptake of Sr ions in meq/g, while the horizontal axis indicates the pH of Sr ions.

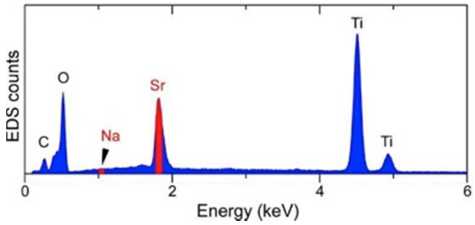

Figure S6. SEM-EDS spectrum of sodium titanate nanowires after immersing in a mixture of $SrCl_2$/NaCl (1/50) aqueous solution. The EDS result reveals that the present sodium titanate nanowires is preferred to uptake Sr^{2+} over Na^+ even in the excess amount of Na^+ in the solution mixing of NaCl and $SrCl_2$ where the concentration ratio of Na^+ to Sr^{2+} is equal to 50, and the peak of Na is not detected as indicated by an arrow.

References

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(4) Leofanti, G.; Padovan, M.; Tozzola, G.; Venturelli, B. *Catal. Today* **1998**, *41*, 207-219.