Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Sodium Titanium Oxide Bronze Nanoparticles Synthesized via Concurrent Reduction and Na^+-doping into TiO_2(B)

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Table S1 Pore characteristics of the TiO_2(B) nanoparticles and the samples reacted with $NaBH_4$ at 350 °C for different time measured by N_2 physisorption.

reaction time /h	a_{BET} [a] /m^2 g^{-1}	$V_{micro-meso}$ [b] /cm^3 g^{-1}	D_p [c] /nm
– [d]	165	0.205	5.5
2	157	0.199	5.5
12	147	0.179	6.3
24	131	0.172	5.5
168	116	0.195	7.2
24* [e]	100	0.148	6.3

[a] specific surface area obtained by the BET method. [b] micro- and mesopore volume obtained from the nitrogen adsorption isotherms at $p/p_0 = 0.99$. [c] mean mesopore diameter obtained by the BJH method. [d] the TiO_2(B) precursor. [e] the Na_xTiO_2-B sample (350 °C for 24 h) after the electric conductivity measurement (heated to 450 ºC under N_2 atmosphere).

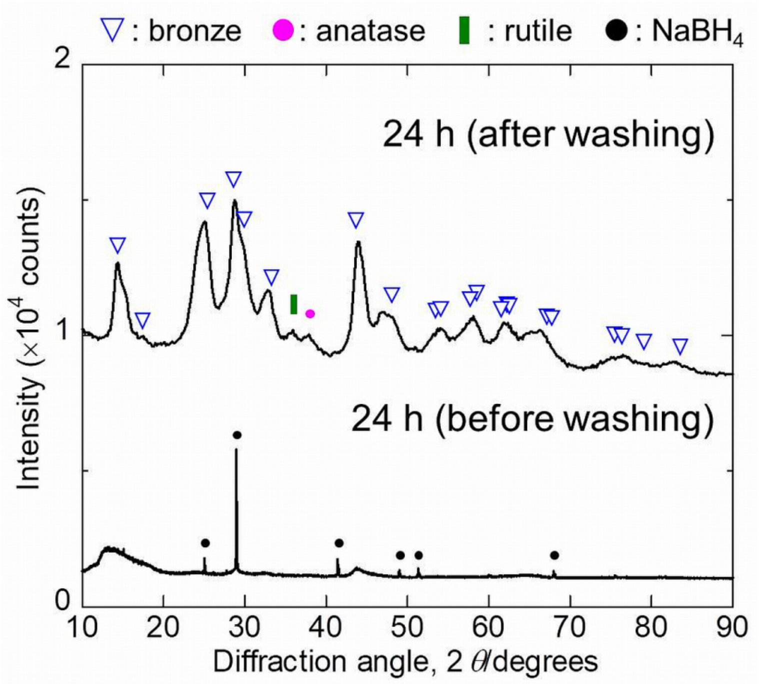

Figure S1 XRD patterns of the samples reduced with $NaBH_4$ at 350 °C for 24 h before and after washing with 0.1 M NH_4Cl/MeOH.

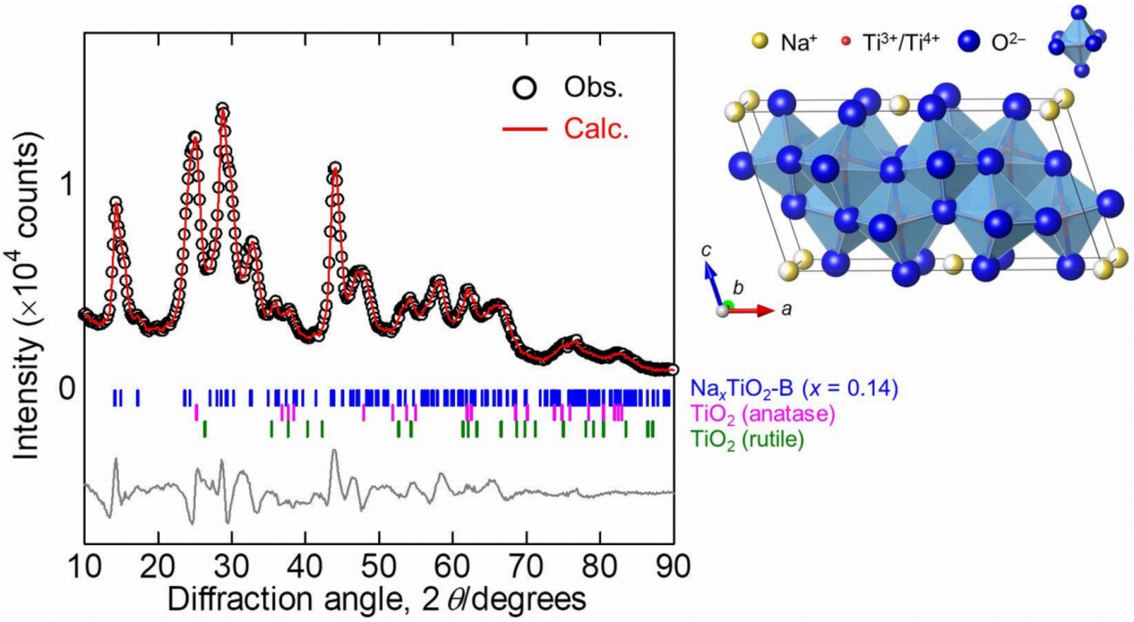

Figure S2 Rietveld refinement result of the Na_xTiO_2-B sample (350 °C, 24 h). The crystal structure of $Na_{0.14}TiO_2$ is also displayed. The top set of Bragg peaks correspond to the $Na_{0.14}TiO_2$ bronze phase, the middle set to an anatase phase, and the bottom set to a rutile phase. The occupancy parameters are fixed during the refinement so that the composition of $Na_{0.14}TiO_2$ is kept. The cell parameters for the $Na_{0.14}TiO_2$ bronze phase is described in Table S2.

Table S2 The detailed cell parameters for the Rietveld refinement result shown in Figure S2.

atom	site	g	x/a	y/b	z/c	B_{iso}
Ti1	4*i*	1	0.298(2)	0	0.711(3)	0.5
Ti2	4*i*	1	0.401(3)	0	0.297(5)	0.5
O1	4*i*	1	0.371(5)	0	0.985(10)	0.1
O2	4*i*	1	0.245(7)	0	0.324(8)	0.1
O3	4*i*	1	0.438(6)	0	0.625(9)	0.1
O4	4*i*	1	0.126(7)	0	0.698(8)	0.1
Na	2a	0.56	0	0	0	0.5

$Na_{0.14}TiO_2$, Space group: monoclinic $C2/m$ (No. 12). Radiation: CuK_α. Lattice constants: a = 12.37(6) Å, b = 3.84(2) Å, c = 6.54(3) Å, β = 107.6(2). R_{wp} = 9.36, R_p = 7.57, and GOF (= R_{wp}/R_{exp}) = 5.56. The occupancy parameter g is fixed for all atoms. The isotropic atomic displacement parameters are fixed during the refinement to avoid falling into unphysical values.

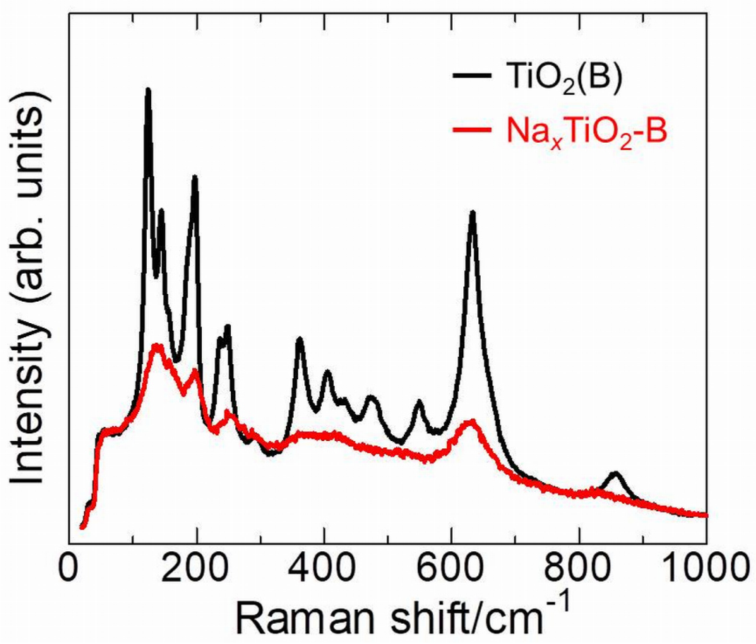

Figure S3 Raman spectra of the TiO_2(B) and Na_xTiO_2-B sample (350 °C, 24 h).

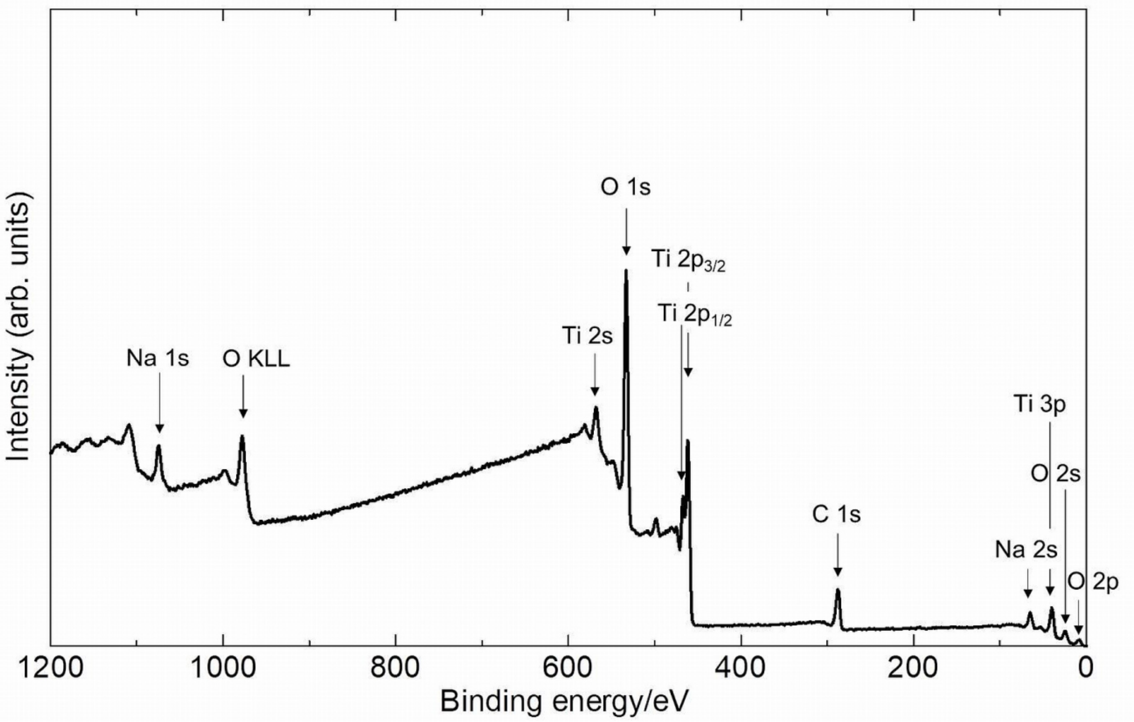

Figure S4 XPS survey spectrum of the Na_xTiO_2-B sample (350 °C, 24 h).

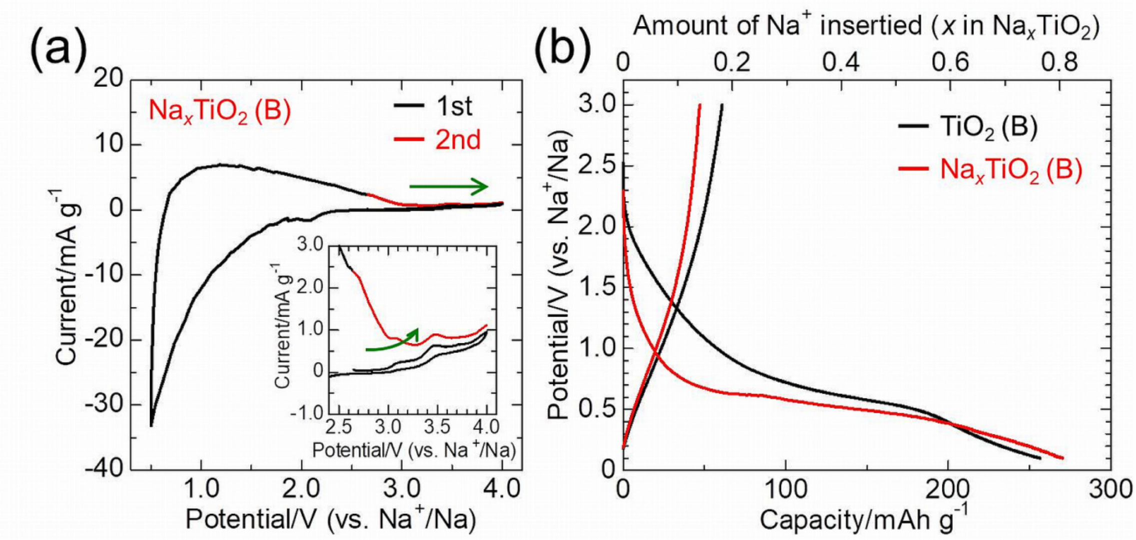

Figure S5 (a) CV curve of the Na_xTiO_2-B electrode in 1 M $NaPF_6$ (EC:DMC = 1:1) with the potential sweep of 0.5–4.0 V (vs. Na^+/Na). The electrode was first subjected to the potentiodynamic sweep from the open circuit potential to 4.0 V (vs. Na^+/Na). (b) Galvanostatic charge and discharge curves for the TiO_2(B) and Na_xTiO_2-B electrodes in 1 M $NaPF_6$ electrolyte with the potential range of 0.1–3.0 V (vs. Na^+/Na) at 10 mA g^{-1}.

Recovery of surface insulating layer for conductivity measurement

The initial Nyquist plot recorded at room temperature (Figure S6) appeared as a large semicircle, which can be attributed to the ionic (mostly proton) conduction through the adsorbed water layer on the particles. This is supported by the fact that the semicircle enlarged as the duration time kept in a stream of dry N_2 gas increased. The slow Na^+-migration is manifested by the abovementioned CV test (Figure S5 (a)). The electronic conductivity was assessed as 1.1×10^{-4} S cm^{-1} from the intercept of the extrapolated semicircle on the real axis in the high frequency region. The fairly low conductivity can be explained by the non-conductive outermost surface layer of each particle, as the XPS study revealed that the surface of the Na_xTiO_2-B was fully oxidized without Ti^{3+} species. It was, however, found that the pellet was dramatically rendered conductive by heating under inert atmosphere. There was no significant change in crystal structure during this measurement, as confirmed in Figure S7.

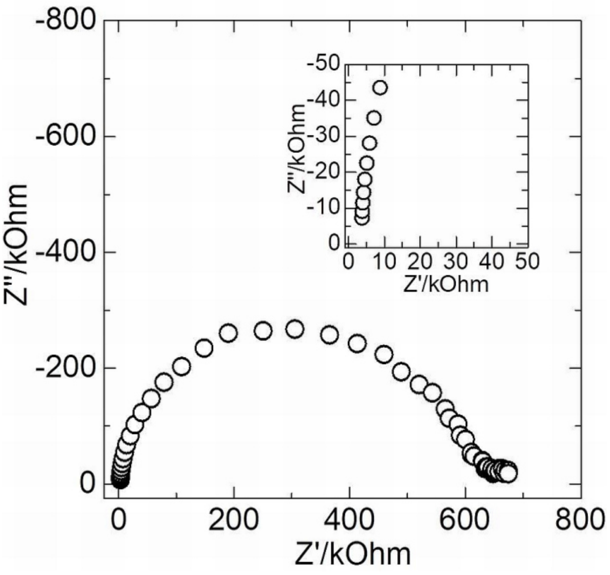

Figure S6 AC impedance spectrum for the pelletized Na_xTiO_2-B nanoparticles recorded at room temperature under N_2 atmosphere before heating.

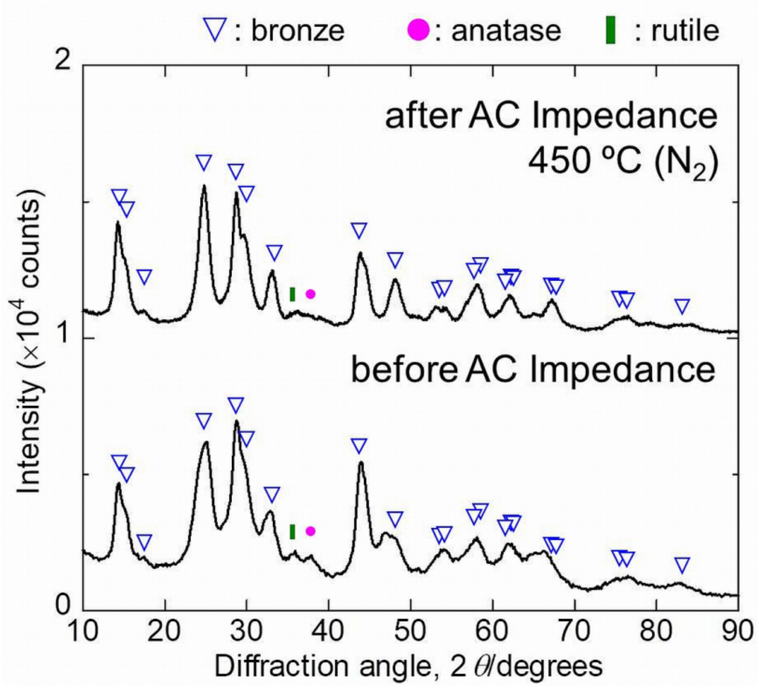

Figure S7 Comparison of the XRD patterns of the Na_xTiO_2-B before and after the impedance measurement.

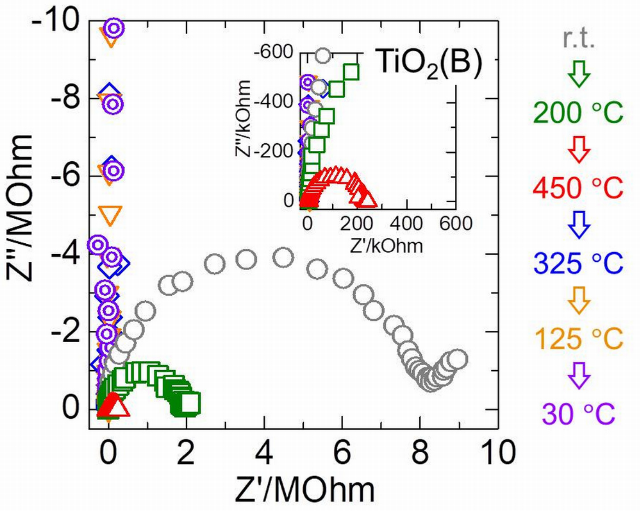

Figure S8 AC impedance spectra for the pelletized TiO_2(B) nanoparticles recorded at varied temperatures under N_2 atmosphere.