

Supporting Information

Synthesis of Nanosheet Crystallites of Ruthenate with α -NaFeO₂ - related Structure and Its Electrochemical Supercapacitor Property

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Material synthesis. α -NaFeO₂ related layered sodium ruthenate, NaRuO₂, was synthesized as a starting material by heating a mixture of Na₂CO₃ and Ru and RuO₂ (2: 1: 3 molar ratio) at 900°C for 12 h under Ar atmosphere. The obtained layered sodium ruthenate was treated with aqueous Na₂S₂O₈ solution to trigger Ru oxidation associated with partial extraction of Na ions. Proton exchange was conducted in 1 mol dm⁻³ HCl, resulting finally in the formation of hydrated layered protonic ruthenate formulated as H_{0.2}RuO₂•0.5H₂O. The acid-treated sample (0.1 g) was added into 25 cm³ of aqueous TBAOH with various concentrations and shaken vigorously for at least 10 days. The concentration of TBAOH was controlled so that the TBA⁺ to H⁺ ratio, where H⁺ is the ion-exchangeable proton content in the layered protonic ruthenate, was varied between TBA⁺/H⁺ = 0.1 and 30 to optimize the exfoliation degree. The resultant dark-green suspensions were centrifugated at 2000 rpm for 30 min to separate the exfoliated nanosheets and the readily sedimenting materials including trace amounts of impurity

Ru metal and also non-exfoliated material. In order to estimate the nanosheet yield, the supernatant was then dried and heated to 500°C in air to convert into rutile-type RuO₂.

A Si wafer was cleaned by dipping in 12 mol dm⁻³ HCl + 24 mol dm⁻³ CH₃OH (1:1 by volume) solution and then in 18 mol dm⁻³ H₂SO₄ solution to obtain hydrophilic surface. The substrate was immersed in an aqueous solution of poly(diallyldimethylammonium chloride) (pH = 9, 2.5 g dm⁻³) for 20 min to pre-coat the surface. Then, it was dipped in a colloidal suspension of negatively charged nanosheets (0.08 g dm⁻³) for 20 min to assemble a monolayer film in which the RuO₂ nanosheets were adsorbed in random azimuth via electrostatic self-assembly onto the substrate surface.

Measurements and analysis. Powder X-ray diffraction (XRD) data were collected by means of Bragg-Brentano-type diffractometers (Rigaku Rint 2000) with Cu K α radiation (λ = 0.15405 nm). Optical absorption spectra for the diluted nanosheet suspensions in a quartz cell were recorded on a Hitachi U-4100 spectrophotometer. A tapping-mode atomic force microscope (AFM; Seiko Instruments SPA400) with Si-tip cantilever (20 N m⁻¹) was used to characterize morphological features of the nanosheets on a flat substrate. In-plane diffraction pattern of the self-assembled film of the nanosheets was measured by a four-axis diffractometer equipped with NaI scintillation counter at the BL-6C of the Photon Factory in the High Energy Accelerator Research Organization.

Electrochemical analysis. A beaker-type electrochemical cell equipped with a working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode was used for the electrochemical measurements. Electrode potentials were referred to the reversible hydrogen electrode (RHE) potential scale. Briefly, 10 mg of

$\text{H}_{0.2}\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}$ was dispersed in 5 cm^3 distilled water and was subject to ultrasonification for 60 min. The nanosheet suspension obtained at $\text{TBA}^+/\text{H}^+ = 10$ was diluted to $\sim 1.9 \text{ g cm}^{-3}$ with ultra pure water ($> 18 \text{ M } \Omega \text{ cm}$). A total of 20 mm^3 of the suspension was then pipetted onto a mirror-polished Glassy Carbon rod (5 mm diameter). A diluted Nafion ionomer solution was then dropped onto the electrode surface to immobilize the active materials. All electrochemical studies were conducted at 25°C in $0.5 \text{ M H}_2\text{SO}_4$. Cyclic voltammetry was conducted between 0.2 and 1.2 V vs RHE with a Hokuto Denko HZ-3000 electrochemical system. The specific capacitance was calculated by averaging the anodic and cathodic charge after 500 break-in cycles at 50 mV s^{-1} . The specific capacitance is reported in unit of Farads per mass of RuO_2 ($\text{F (g-RuO}_2)^{-1}$) to allow uncomplicated comparison between different materials.

Chemical analysis. The molar ratio of Na to Ru after the oxidative de-intercalation of Na^+ was estimated by energy dispersive X-ray (EDX) analysis. NaRuO_2 was used as standard material for X-ray intensity ratio of Na to Ru. Mass loss up to 400°C measured by thermogravimetry (Rigaku Thermo Plus TG 8120) provided information on the proton, oxonium and water content in the oxidized and completely protonated derivatives.

Figure S1 Logarithmic XRD data for (a) NaRuO₂, (b) oxidized derivative of (a), and (c) protonated derivative of (b); black circles show peaks due to Ru metal.

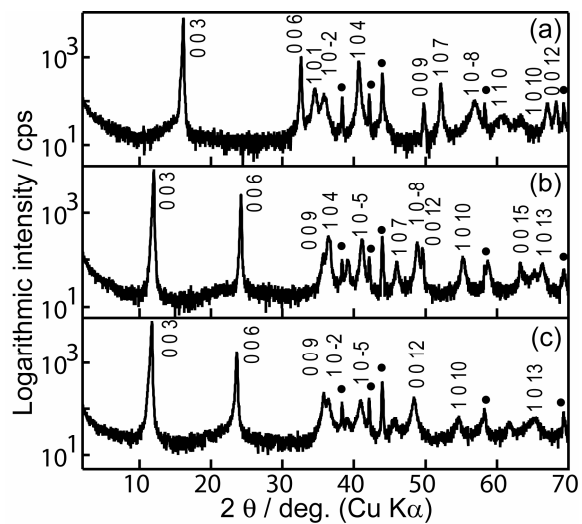
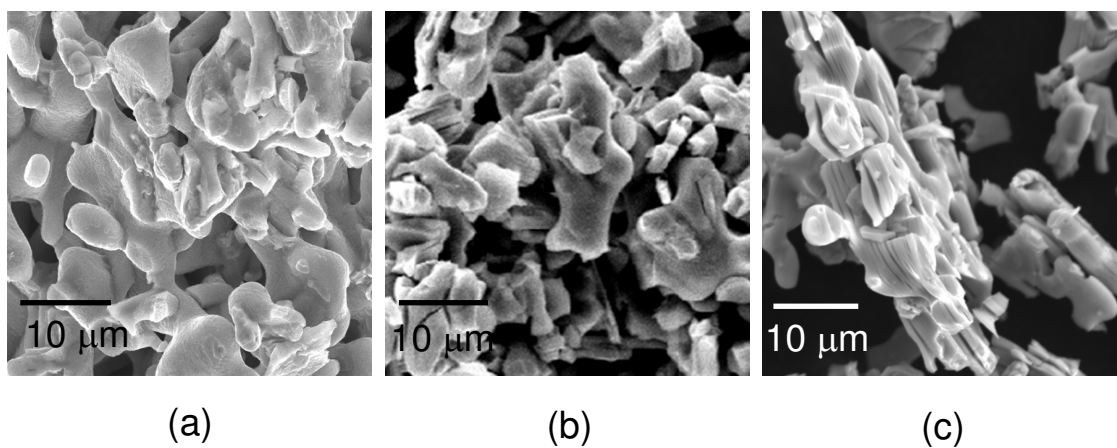
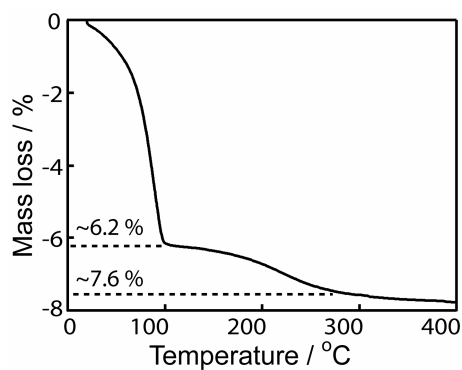


Figure S2 SEM images for (a) as-synthesized material, (b) oxidized form and (c) completely protonated form.



The typical lamellar morphological of the parent NaRuO_2 remains basically unchanged through the oxidation and ion-exchange processes.

Figure S3 Thermogravimetry curve of completely protonated ruthenate under flowing dry air.



Intense weight loss up to 100°C, ~6.2%, can be attributable to the dehydration process of physically and/or chemically adsorbed water. The gradual subsequent decrease of ~1.4%, may be due to release of protons accommodated in the layered gallery as water molecules. Transformation to rutile-type RuO₂ after thermogravimetry was confirmed by XRD. Combined with the fact that the Na⁺ after acid treatment was negligible (by EDX), the chemical formula can be roughly described as H_{0.2}RuO₂·0.5H₂O.

Figure S4 Crystallographic data for $\text{H}_{0.2}\text{Ru}^{3.8+}\text{O}_2 \cdot 0.5\text{H}_2\text{O}$.

| <i>h</i> | <i>k</i> | <i>l</i> | <i>d</i> | Intensity |
|----------|----------|----------|----------|-----------|
| 0 | 0 | 3 | 7.52 | 100 |
| 0 | 0 | 6 | 3.753 | 25 |
| 0 | 0 | 9 | 2.500 | 20 |
| 1 | 0 | -2 | 2.467 | 20 |
| 1 | 0 | -5 | 2.205 | 10 |
| 0 | 0 | 12 | 1.875 | <1 |
| 1 | 0 | 10 | 1.6794 | 1 |
| 1 | 0 | 13 | 1.4277 | <1 |

$a = 0.2919(2) \text{ nm}$, $c = 2.249(1) \text{ nm}$