

Thermally stable proton conductivity from nanodiamond oxide

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Experimental Section

All chemicals used are analytical grade and used without further purification. Commercially available Dinnovare Cluster NDs were obtained from Daicel Corporation, Tokyo, Japan.

Preparation of NDOx: The Nanodiamond oxide (NDOx) powder was prepared using modified Hummer's oxidation method of ND.^[1] In a typical preparation, 1 g of Nanodiamonds stirring mixed with 1 g of NaNO₃ and 48 mL of H₂SO₄ under ice bath for 15 minutes keep the temperature under 0 °C. KMnO₄ was slowly added (3 g of finely mesh) to the solution and keep the temperature bellow 20 °C under stirring. Increase the temperature at 35±3 °C after half an hour and keep stirring for 30 minutes. Then add 180 mL of Milli-Q water and the temperature will increase gradually until reach 95±3 °C. Keeps stirring for additional 30 minutes. Add 400 mL of Milli-Q water. Finally add 12 mL of 30% H₂O₂ to convert all permanganates and manganese dioxide into sulfates. Then centrifuge the solution (3000 rpm for 10 minutes). The precipitate then washed with 5% HCl solution (1 times) and water (3 times). It was re-dispersed in water (0.9 mg/mL) by 2 hours of sonication. Lastly centrifuge the solution at 4000 rpm for 1 hour.

After the preparation, NDOx was dried in a vacuum at 30 °C for 12 hours.

Characterization: The structure and morphology of the materials synthesized were characterized using X-Ray diffraction, Raman Spectroscopy, Fourier Transform Infrared (FT-IR), Thermo Gravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM).

Proton Conductivity Measurement: The proton conductivity measurement of Nanodiamond (ND) and NDOx were measured using four probe Alternating Current (AC) methods connecting with an impedance analyzer (Solartron 1260, TOYO Corporation) over the frequency range 1 Hz to 5 MHz. The proton conductivity measurement was conducted using the out-of-plane direction. After compression, the pellet was placed between two copper electrodes and made sandwich-like. Proton conductivity was measured in an incubator under humidity and temperature control (IW223, Yamato Scientific Co.). For thermal stability measurement, the NDOx pellet was annealed at 373 K for 1 h and measured proton conductivity at 298 K, 90% RH. The procedure then repeat with the annealing the pellet at 473 K for 1 h.

The proton conductivity is calculated as follows,

$$\sigma = d / (R \cdot S)$$

Where R is Resistance (Ω), S is the sectional area (cm), and d is the distance between electrodes (cm).

Table S1. Peak table obtained from XPS analysis

	C 1s						
	C sp2	C-H	C sp3	C-O	O 1s	N 1s	Cl 2p
ND	8.34 %	21.62 %	54.66 %	4.93 %	8.71 %	1.42 %	0.32 %
NDOx	8.38 %	19.54 %	50.19 %	8.24 %	11.54 %	1.82 %	0.30 %

Table S2. Proton conductivity different NDOx conducted at 298 K, 90% RH.

Materials	Proton conductivity σ_{\max} ($S \text{ cm}^{-1}$)		
	Without Drying	Drying at 373 K	Drying at 473 K
NDOx	3.0×10^{-5}	2.6×10^{-4}	2.8×10^{-5}

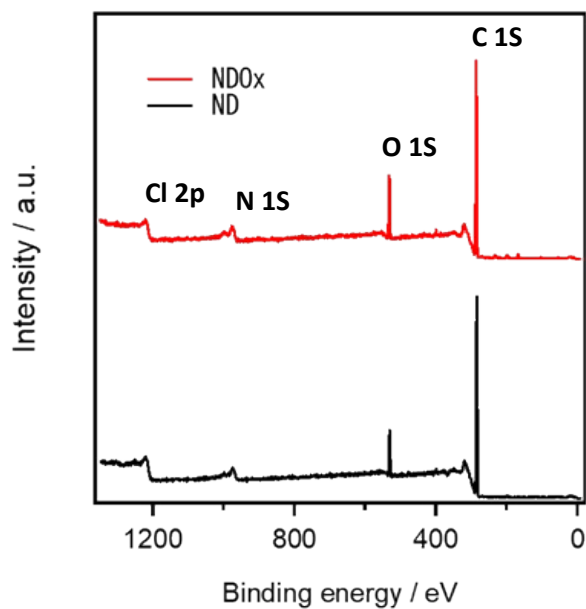
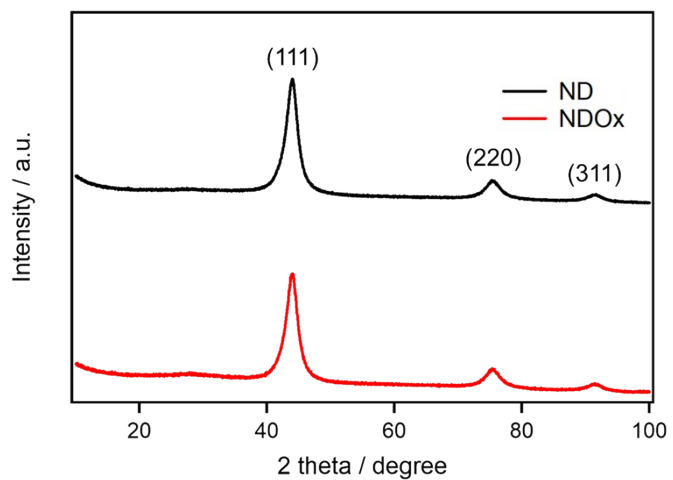


Figure S1. PXRD patterns of ND and NDOx

Figure S2. XPS survey spectra of ND and NDOx

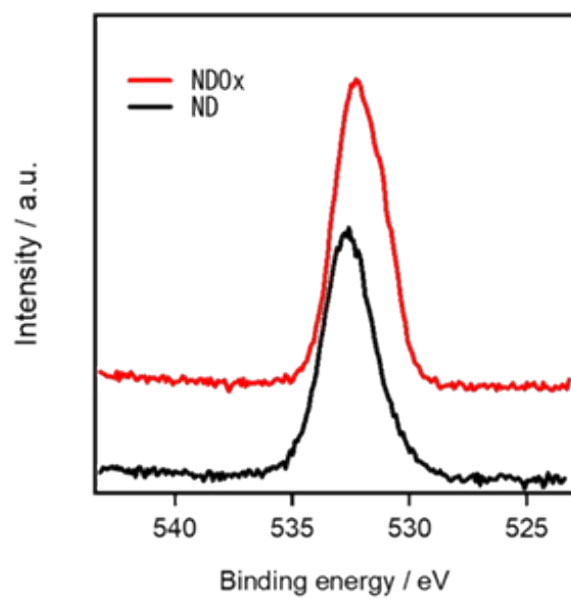


Figure S3. XPS data of O1s ND and NDOx

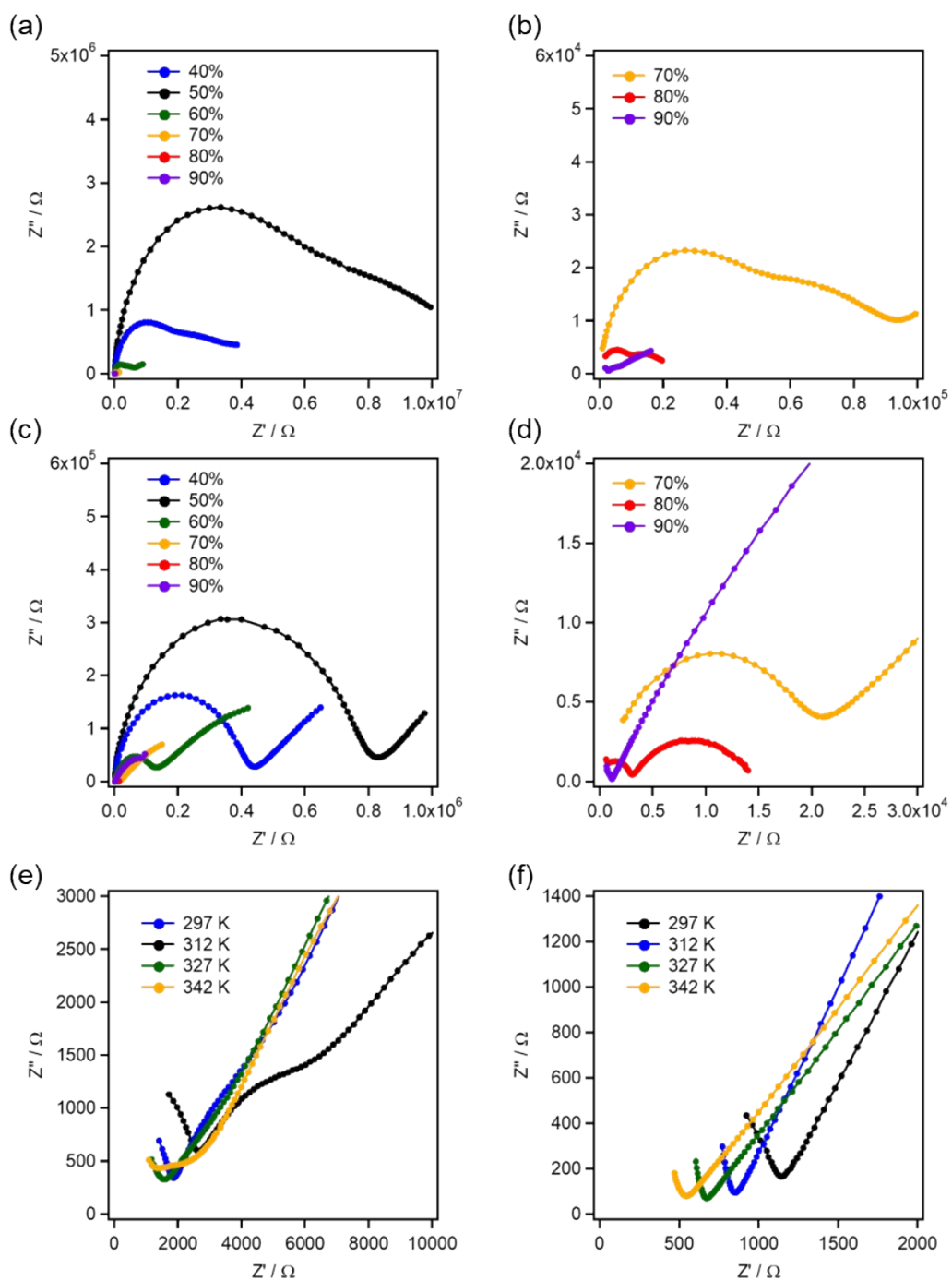


Figure S4. Nyquist/cole-cole plots (a), (b) for ND and (c), (d) for NDOx under different humidity (40-90 %) at 297 K; (e) for ND and (f) for NDOx under different temperature (297-343 K) at RH 90 %.

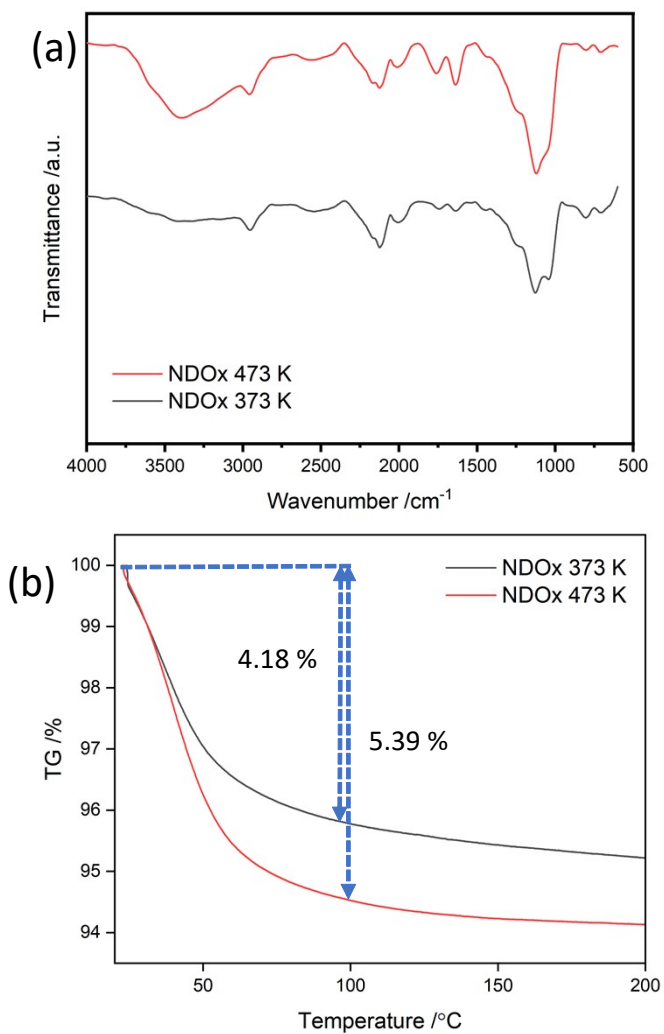


Figure S5. Characterization of NDOx after annealing at 373 K and 473 K (a) FTIR spectrum, and (b) TGA measurement.

References

- 1 M. Fukuda, M. S. Islam, Y. Shudo, J. Yagyu, L. F. Lindoy and S. Hayami, *Chem Commun*, 2020, **56**, 4364.

